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JOURNAL

THE CHEMICAL SOCIETY.

I.—*On the manner in which Cotton unites with Colouring Matter.*

By Walter Crum, F.R.S.

SECOND MEMOIR.

In the year 1843, I published a Memoir* on the manner in which cotton-fibre unites with colouring matter in the process of dyeing. I endeavoured to show that the combination which there takes place is not the result of chemical affinity, as was at that time universally understood, but that the union is a mechanical one; and, among other illustrations, I described various processes of dyeing in which the mechanical union is in different ways effected.

Since that period, much has been said in opposition to the views then advanced, but, generally with a very imperfect apprehension of them. I had indicated but a few of the facts which led to the conclusions then arrived at, leaving unexplained other facts and processes which have been supposed to contradict them.

The subject is sufficiently important to demand the more full and systematic statement on which I propose now to enter,—repeating, necessarily, some of the illustrations formerly adduced, and taking advantage at the same time of certain new facts with which I have since become acquainted. In this way I conceive I shall best answer the particular objections, and correct the misstatements that have been made. I shall describe the processes to be alluded to in such a manner that the chemist who may not hitherto have attended to this technical branch of his science will

* Proceedings of the Philosophical Society of Glasgow, i, 98. Phil. Mag., vol. xxiv, April, 1844. Ann. Ch. Pharm., lv, 220.

have no difficulty in following the statements; and from the new light in which the subject is viewed, I trust they will not be without interest, even to those who are already acquainted with the general facts.

In my original communication, I gave a slight history of the old mechanical and the chemical explanations of dyeing. The early views entertained by Macquer, Hellot, and Le Pileur d'Apligny, with their theory of pores, incomplete and inconsistent as they were, and wanting the support of facts which we now possess, gave way at once to the chemical theory of Bergman. In his treatise on indigo, in 1776, that chemist attributed to cotton the power of elective attraction, which had just been promulgated for acids and bases, and in this reasoning from analogy he was followed by Macquer, Berthollet, and all other writers on the subject. But no one who is at all conversant with the rationale of the processes of dyeing, and with the laws of chemical combination as they are now understood, can examine the question without arriving at an opposite conclusion.

Cotton-wool in the bleached state, that is, when freed as much as possible, by the action of alkalies, hypochlorites, and acids, from foreign ingredients, may be considered as pure woody fibre, or cellulose $C_{12}H_{10}O_{10}$. It is one of the most inert of vegetable bodies. In the textile fabric it is capable of having incorporated with it, in all proportions, a multitude of different substances without changing its own or their physical or chemical characters, except by holding them against mechanical efforts to wash away, or otherwise to separate them, but yielding them up to their proper solvents as readily as they could be taken from a surface of glass.

We know only two examples of chemical combination into which cotton-wool, without total disintegration, is capable of entering; these are its compounds with nitric acid and with potash or soda. When cotton-wool is made to imbibe nitric acid by the gun-cotton process, a true chemical combination is formed, in equivalent proportions, but the characters of both constituents are completely changed, and the cotton $C_{12}H_{10}O_{10}$ has, as I find, 3HO replaced by $3NO_5$ forming the compound $C_{12}H_7O_7$, $3NO_5$*. Or the substitution may be stated thus:—

$$C_{12}H_{10}O_{10} + 3NO_5 = 3HO + C_{12}H_7(NO_4)_3O_{10}$$

* I have been represented, by Messrs. Porrett and Teschemacher (*Mem. Chem. Soc.* iii, 261) as taking a mechanical view of the nature of gun-cotton, but I cannot discover on what grounds. In my paper on the Nitrates and on Gun-cotton

The combination with soda in Mercerised cotton, if it does exist, is not so stable, and the ultimate constituents of the cotton undergo no change; but, according to Dr. Gladstone, there is a chemical combination $C_{24}H_{20}O_{20},KO$, which, although decomposible by water and by carbonic acid, resists washing with alcohol. All other substances with which cotton has been made to unite, including those which form its various dyes, retain the colour and all the other properties which they possessed in a separate state. Their union does not materially affect even the degree in which they resist the external influences of light, or of alkaline and other re-agents.

The attraction which is attributed to porosity or capillarity we know to be an attraction of surface, but it is one in which, in consequence of its structure, the absorbing body has its power of attraction for that which it imbibes immensely increased. The term capillarity gives but a faint idea of the disproportion between the extent of surface of the cell which constitutes a pore in the woody fibre and the almost mathematical line or point of matter which that cell is capable of containing. From the experiments of Saussure, we learn that boxwood charcoal absorbs a quantity of carbonic acid 56 times greater than the capacity of its pores, which implies the existence of a large proportion of it in the liquid state. Other porous bodies have similar properties;—raw silk, linen thread, the dried woods of hazel and mulberry, although they were found to condense but a small quantity of carbonic acid, took up 70 or 100 times their bulk of ammoniacal gas; and Saxon hydrophane, which is nearly pure silica, absorbed 64 times its bulk of that gas. The gas does not enter into combination with the solid which absorbs it: the air-pump alone destroys their union.

The power which charcoal possesses of attracting to its surfaces certain solid bodies which are dissolved in water is equally well known. Bone-charcoal removes the colouring matter from the brown solution of tartaric acid, and from syrup in the refining of sugar. It precipitates lime from lime-water, and metallic oxides from their solution in ammonia or caustic potash; but no chemical union has ever been supposed to exist between the charcoal and

(Proc. Phil. Soc. of Glasgow, ii, 163, April, 1847.—Phil. Mag., vol, xxx, June, 1847. —Ann. Ch. Pharm., lxii, 233) I assign to it the constitution in the text, as the result of my own experiments. I have always attributed the difference between my analyses of gun-cotton and those of others, to the purifying process to which, in the former case, the cotton was subjected.

these gases or solid matters. It is well known to be chemically indifferent to all such bodies.

Mitscherlich calls the force which produces such remarkable effects upon the gases, an action of contact, or an attraction of surface, and he calculates the extent of surface, in proportion to the mass which it attracts, as a measure of the force which it exerts. But it is something more, or at least the fact may be more strikingly stated. The same, or even a larger amount of surface unenclosed, does not exert an equal power. Saussure, in his valuable paper on the absorption of gases, informs us that charcoal from boxwood in the solid state absorbs twice as much common air as when reduced to powder. The condensation of gases in the solid charcoal goes on, he conceives, in the narrow cells of which it is composed, and is analogous to the rise of liquids in capillary tubes. But when we pulverise a body containing such cells, we open and destroy a large portion of them. While, therefore, we increase the actual amount of surface, we increase in a much larger proportion the amount of the fluid on which it acts, and thereby diminish the intensity of the action.

It was these remarkable facts, as described by Saussure, Graham, Bussy, Mitscherlich, and others, and not the crude mechanical theories of the last century, that drew my attention to the similarity of the action of cotton-wool in several of the processes of dyeing.

The cotton-fibre was first figured and published by Mr. Thomson, of Clitheroe, in 1834, in his interesting work on the "Mummy Cloth of Egypt," from drawings by Mr. Bauer.* These drawings gave an idea of the flax, and of the ripe cotton-fibre, sufficiently true for Mr. Thomson's purpose, but in many respects they were most inaccurate. When, some time afterwards, the defects were pointed out to Mr. Thomson, he employed Mr. Varley, of London, again to subject these fibres to the microscope, and have figures of them engraved, intending, besides, to write a continuation of his memoir on the mummy cloth. This he did not live to complete, but some engravings were made and published in No. 2 of the "Classical Museum," together with a copy of the first paper. Mr. Bauer represented the cotton-fibre in the unripe state as a perfect cylindrical tube; and, when ripe, as a cylinder collapsed longitudinally in the middle, and twisted.

* Annals of Philosophy for June, 1834, and Ann. Ch. Pharm. for January, 1849, lxix. 128.

By the use of instruments more perfect than that employed by Mr. Bauer, we find the mature cotton-fibre to be a shrivelled, irregular, partially twisted cylinder, of about $\frac{1}{1000}$th of an inch at its greatest diameter; and if we take the middling American at $1\frac{1}{4}$ inch long, a cord of $\frac{1}{8}$ inch diameter and 13 feet long would give an idea of its relative dimensions. It is not, however, of equal thickness. Towards the end farthest from the seed it gradually diminishes like the tape-worm, to about one-fifth of its greatest diameter, and there its form is more nearly cylindrical and straight.

Under the microscope, the walls of these tubes do not exhibit openings of any kind which can be taken for lateral passages, but it cannot be doubted that like other ligneous matter they are not impervious to fluids. Dr. Carpenter mentions as one of the most remarkable properties of vegetable membrane, its power of allowing fluids to pass slowly through it, even though no visible pores or apertures can be detected in it.

Substances applied to cotton as dyes, or for the purpose of attracting dyes, become fixed in the cotton-fibre in two different ways.*

I. They are attracted and precipitated from their solutions by the pores of the cotton. Or,

II. They enter these pores in combination with an acid or other solvent, and in a state of solution; and are there fixed, not by an effect of porosity, but by the subsequent removal of their solvent, or by other means which render them insoluble in water.

Class I.—Attraction by Porosity; or, processes depending essentially upon attraction of surface. I shall describe as an example:—

The Indigo-dye.—When a pound of finely divided indigo, mixed with a hundred and fifty pounds of cold water, is kept for sometime in contact with hydrated protoxide of iron and quicklime, the indigo is gradually dissolved, and there is formed an olive-yellow solution, from which the indigo may be reproduced and precipitated in its original blue state by oxidation, through exposure to the atmosphere.

* Pigments and other colouring matters which are fixed upon cotton by means of albumen, oils, &c., are not here treated of.

When a piece of cotton cloth is immersed in a solution of any salt or other substance which is indifferent to it, the solution is imbibed by the ordinary hydrostatic capillary force; and when the cotton is withdrawn, the same quantity of salt adheres to it whether the period of immersion be long or short. But when a similar piece of cloth is dipped in the solution of indigo just described, there is also exercised a power of decomposition and precipitation by which the indigo is gradually attracted to the cotton from the solution around it, so that if the immersion be continued for a quarter of an hour, it becomes loaded with ten times as much indigo as another piece which has been withdrawn immediately after its immersion. If successive portions of cotton be employed, the solution becomes robbed in this way of all its indigo. Before exposure to the atmosphere (which, by oxidising, restores its blue colour), the indigo is attached to the fibre in its yellow insoluble state.

The force here exerted appears to be analogous to that which enables charcoal and dried wood to precipitate bodies in similar circumstances, and there seems no greater reason for supposing that a chemical union has taken place in the one case than in the other.

Other examples of the first class will be given after the second has been described.

CLASS II.—Processes where the mordant or dye has entered and become fixed within the fibre, independently of attraction. *Example:* Madder colours, with mordants of acetic solutions of iron or alumina.

It is proper here to premise that no substance can be made to adhere effectively to cotton, which has not originally been applied to it in a state of solution. However impalpable the insoluble powder or the precipitate which we employ, mixing it with gum or other mucilage, and so placing it upon the cloth, it cannot be fixed,—the washing and beating which removes the gum removes also the insoluble matters which accompanied it.

The substance which produces the madder-purple colour upon cotton is a lake, or black substance, which, by great attenuation, becomes purple. Being insoluble in water, it cannot, as we have seen, be made, ready formed, to attach itself to cotton. But it is composed of two ingredients, viz., oxide of iron, which can be dissolved in water by the intervention of an acid, and the colour-

ing (or rather colourable) matter of madder which is itself soluble in water. The practice is, first to apply the iron in solution; and when that is rendered insoluble in the fibre, to give it the opportunity of drawing to itself, through the membrane which contains it, the soluble madder.

The iron employed in this way to attract the dye-stuff, is called a mordant. Metallic iron dssolved in pyroligneous acid is the particular preparation used as a mordant for a madder purple dye. It is essentially an acetate of protoxide of iron. When a solution of this salt is applied to cotton, it is received into the pores of that body by common capillary attraction, but its oxide is not appropriated by the fibre as indigo is. A stream of water being sufficient to remove it, it is evident that cotton has not the power of separating the protoxide from its acid, even when that acid is the acetic. But if, after the solution of pyrolignate of iron has been applied to the cotton fabric, it be allowed to dry, and then exposed to an atmosphere slightly warm and moist, the acetic acid gradually escapes, in proportion as oxygen is absorbed, and the iron, in the state of an insoluble hydrated peroxide, remains.

But as insoluble matters cannot pass into the interior of the fibre from without, so, when a substance has once entered that fibre, or its pores, in a state of solution, and has become precipitated within these enclosures, it is equally impossible for the precipitate to return. It is entrapped within the body of the fibre, or its tissue, and becomes fixed there.

It will be seen that this precipitation and imprisonment of the oxide is no case of attraction, either chemical or mechanical. It is a case of chemical decomposition in which the cotton acts the part only of a vessel to receive the materials. The same solution spread thinly over glass, and placed in similar circumstances, undergoes the same decomposition. The greater subdivision of the salt may, indeed, in the case of the vegetable fibre, accelerate its decomposition; but a slight elevation of temperature in the other case is sufficient to compensate for the greater exposure in the cotton fibre.

The inferences that may be drawn are:—

1st. That the pores, whether larger or smaller, receive the solution of iron by ordinary hydrostatic capillary attraction.

2nd. That while within these cavities or vessels, whatever be their form, the salt is peroxidised and decomposed; and

3rd. That the result of the decomposition,—an insoluble oxide,

—is left there by the volatile acid, which, by its solvent power, had placed it in that position.

In pursuing the process, the cloth which is thus furnished with its mordant of iron is first passed through hot water, with certain precautions which need not here be detailed, and washed, to remove any unfixed mordant; after which it is ready to be dyed. For that purpose it is made to traverse for a couple of hours a vessel of water, throughout which madder in powder has been distributed. Heat being gradually applied, the colouring matter of the madder dissolves, slowly indeed, and by little at a time, but, being soluble, it has no difficulty in passing into the fibre which encloses the oxide of iron, and there uniting with it. The resulting compound is the purple lake.

This last process is a purely chemical one, in which the oxide of iron forms a true combination with the colourable matter of the madder, the cotton attenuating the iron to a prodigious extent, and placing it in circumstances the most advantageous for forming a lake with this dye-stuff.

Having thus received the dye, the fabric is subjected to a process of soaping in boiling water, by which its colour is much reduced in depth, and brightened in shade.

Having formed the idea, that no portion of the dye but that which is held most firmly within the cotton-fibre could bear the severe soaping operations to which this class of prints is subjected, I formerly described a piece of dyed cotton as consisting of a set of colourless bags, containing coloured substances, and in so far resembling the cells of natural flowers; but the statement was incomplete, and the proof rested to some extent upon theoretical considerations, until the opportunity occurred of observing the effects of the same process upon "*dead cotton.*" And as the behaviour of this substance in such circumstances throws much light upon the question we are now discussing, I shall proceed to give some account of it.

Dead Cotton.—In May, 1848, Mr. Thomson, of Primrose, received from Mr. Daniel Kœchlin, of Mulhouse, some specimens of a purple-ground printed calico, each of them containing a portion of cotton which was white, although it had been subjected to the same treatment by which the rest of the cloth, and even the threads which crossed the white ones, were uniformly dyed. The white part of the thread was usually thicker

than the rest, and little more than a quarter of an inch long. The whole fabric had been thoroughly bleached before printing, so that its white thread contained no grease or other impurity that could have mechanically resisted the colouring matter. Mr. Kœchlin at the time suggested that it might consist of unripe cotton, and might want the hollow of the perfect fibre. Both in France and in this country it is called "*dead cotton.*" Mr. Thomson kindly transmitted me the specimens for examination, and my first observations on the subject were published in 1849, in the "Proceedings of the Philosophical Society of Glasgow."*

On placing it under the microscope, I found the cotton which had thus resisted the dye to consist of very thin and remarkably transparent blades, some of which were marked or spotted, while others were so clear as to be almost invisible, except at the edges. These fibres are readily distinguishable from those of ordinary cotton by their perfect flatness, not having the vestige of a cavity even at the sides, and by their uniform as well as great transparency. They are broader than the usual fibre, and they show numerous folds, both longitudinal and transverse.

On afterwards searching among the motes, or hard portions, called droppings, which are rejected by the picking machine in the preparation of raw cotton wool for spinning, I found what proved to be the same fibre, in the form of a small matted tuft of a shining silky lustre, several of which enclosed the fragment of a seed, or perhaps an imperfectly formed seed. The fibres are short, and have little tenacity. Small tufts, however, do occasionally pass the sifting process of the picking machine; and then these fibres, being too short to be teased out in the carding engine, or properly drawn into threads in the subsequent operations of cotton-spinning, remain as minute lumps, or knots, entangled among the fibres of the thread of good cotton, giving great annoyance to the spinner of fine yarns, and appearing as white specks upon a woven and dyed fabric.

In the month of June last, I was favoured by Mons. Le Play, at the request of Dr. Playfair, with a number of specimens of the dried fruit of the cotton plant in various stages of maturity, from the Algerian collection in the International Exhibition, and was thereby enabled to ascertain the real nature of the peculiar fibre.

1st. I found that the contents of every capsule which had not

* Vol. iii. p. 61; also Philosophical Magazine, vol. xxxv. November, 1849.

opened, and of those which had but slightly opened when cut from the plant, consisted, in each cell, of a closely packed solid mass, without elasticity, which, however, could be teased out into fibres presenting under the microscope the same flat, glassy, broad appearance exhibited by the dead cotton fibre already mentioned.

2nd. In capsules more fully developed, the ordinary cotton appeared where it had pushed its way outwards, and assumed the woolly form; while the seeds in the same cell nearer the calyx and still confined, were clothed with the solid mass, chiefly consisting of the glassy, though somewhat less transparent, fibre.

3rd. The glassy fibre frequently appeared in pods of ripe cotton, in spots where discolouration showed that an injury had taken place before maturity.

4th. Small portions glazed and satiny, which proved to be dead cotton, though not discoloured, were seen, but rarely, on the outer part of the wool of a well clothed ripe cotton seed.

5th. We must add to these sources of dead cotton the small glazed tuft already mentioned as found in cotton bales, and appearing to have separated from the stem through which it derived nourishment, while the other seven or eight seeds in the same cell went on to maturity.

6th. The glassy fibre is broader—often one-half broader—sometimes even twice as broad as the ripe fibre.

7th. A distinct gradation is perceptible under the microscope in different specimens, from the pure and spotless glassy fibre in the least mature cotton, to the comparatively dense and opaque ripe cotton.

8th. By the kindness of Mr. Henry Cole, I was enabled to examine some dried specimens of New Orleans cotton, also in various stages of maturity, in the South Kensington Museum. The chief difference from the Algerian was that in the American plant the fibre is more mature at the same stage of development of the pod.

I searched for a living plant in the hope of finding the cylindrical fibre filled with sap, as sketched by Mr. Bauer; hoping also to watch the process of thickening of the cell-wall which goes on during the ripening of the fruit, but I could find no fruit-bearing specimen of the plant in any of our public gardens, and nothing has till now been written on the subject. I was kindly furnished by Mr Morris Pollok, of Glasgow, with a cotton-pod from his own garden, nearly full grown, but still green and unripe. Its

fibre did not differ much from the dried unripe specimens from Algeria.

Although the general microscopic appearance of the unripe fibre is that of a single blade, we know from its subsequent history that it is a flattened tube, and therefore double. There is the same indication from the markings upon its surface. These usually consist of short and faint irregular lines—the effect apparently of creases or corrugations of the membrane—which are spread pretty generally over the fibre, and in the direction of its length. At the ends, however, where the fibre has been torn asunder, portions of it may be seen where the membrane is thinner, and the markings fewer than elsewhere; evidently from one side having been torn away from the other. These appearances will be found represented in drawings which are in course of preparation.

This glassy fibre corresponds with the *cellular membrane*, which Professor Henfrey ("Micrographic Dictionary," article VEGETABLE CELL) describes as a primary formation in young plants, and as consisting of a thin structureless pellicle, possessing a considerable degree of toughness, and a certain amount of elasticity, having also no perceptible orifices, and yet readily permeable by water.

During the stay which I made in London in June and July, I was fortunate enough to secure the assistance of Mr. Tuffen West in the renewed microscopic examination I had undertaken of the cotton-fibre, and I take this opportunity of acknowledging my obligations for the valuable suggestions he afforded me in completing the investigation, as well as for his assistance in commencing the drawings which accompany this paper.*

After numerous attempts at obtaining a view of the interior of the mature cotton-fibre, which were attended with only partial success, I procured at last a number of transverse sections, showing tubes of every variety of form, and discovering in the most interesting manner the nature of their contents.

This examination was much facilitated by the employment of dyed as well as undyed specimens of cotton. The fabric from which the most successful of these sections were obtained had been dyed of a red colour, by incorporating it with an aluminous lake of madder. The cotton was first mordanted with alumina by soaking it in a solution of the submuriate of that earth. It was then dyed

* I regret that the illness of Mr. West has prevented me from completing these drawings in time for the present number of this journal

in madder in the usual way, after which it was subjected to the cleansing and brightening which is produced by the action of a hot solution of soap. I was not a little surprised to find the fibre almost entirely filled up with secondary deposit, the internal cavity being reduced to a comparatively small chamber in the centre. Some of the cross sections of these fibres were found under the microscope to be irregular circles, exhibiting the ends of tubes nearly cylindrical. Many of them showed no cavity at all, their whole interior being a mass of red matter, apparently deepening in shade towards the centre. Others were oval-shaped in various proportions of length and breadth, showing generally a small central cavity, circular or long, corresponding to the external outline of the tube. These sections showed also occasionally a fibre hollowed on one side and rounded on the other, with a cavity of corresponding form in the centre. The central openings are sometimes only discernible as dark specks or lines in the centre of the disk, or there appears a dark line surrounding a central cavity of a paler hue. I must add that I have not observed any cavity altogether destitute of colour in a tube otherwise filled with red matter—a fact which must be attributed to the difficulty of forming sections so thin as to allow the opening to be seen in a straight line from end to end, and to the rough spongy character of the deposit which forms the boundary. Diagonal slices frequently occur confirming the apparent character of the disk.

There is a remarkable resemblance between the cavities I have endeavoured to describe and the apertures which appear in the more readily formed cross sections of the liber-fibres of hemp and flax, as these have already been delineated by Mr. Tuffen West, in the "Micrographic Dictionary," and, by the same artist, in a late article on "Cotton," by Dr. Lankester, in the "Popular Science Review."

Longitudinal sections of the dyed cotton-fibre show more perfectly the differences which occur in the amount of colouring matter taken up by the different fibres. These are found in every variety, from the perfectly flat, riband-like, and consequently colourless fibre, like that which is found in the unripe pod, gradually expanding in proportion to the quantity of new deposit which it receives, until it becomes swelled out into the nearly perfect cylinder; and similar differences occur, though to a smaller extent, in the same fibre. Bleached cotton is much more transparent than the unbleached, and takes up in the same circumstances much less dye,

—a large proportion of the secondary deposit having apparently been removed from it by the action of alkalies in the process of bleaching.

From these observations it would appear that the primary cellular membrane, as found in the unripe plant, never acquires the power of absorbing colouring matters; that its only purpose in dyeing is to enclose the soft and granular secondary matter which becomes deposited within it while in progress towards maturity, and that that secondary matter has alone the faculty of attracting those mineral and vegetable substances which are either dyes themselves, or which form dyes by attracting and combining with other bodies. The colourless character of the external membrane, however, is not to be discerned in the well dyed fibre, just as we cannot by mere inspection detect the colourless character of the cell which contains a coloured juice in the natural flower, or like a thin tube of glass which in appearance partakes also of the colour of any fluid that it may contain. It will also be seen from those statements that the deposition of secondary matter within its cell does not commence until after the pod has begun to open, and when it has grown therefore to its full size. These new deposits, says Professor Henfrey, speaking of other plants in which similar substances are formed in quantities sufficient to admit of separate examination, are layers of cellulose, like the primary membrane.

Here, then, are two specimens of cellulose, having the same chemical composition, and subjected to the same process of dyeing, one of them, which is formed by deposition in a manner to expose the greatest amount of surface, and enclose the greatest number of minute cavities, having the power of decomposing certain solutions and entrapping mordants, while the other, a hard, compact, polished membrane, is without appreciable action upon mordants or dyes. The relationship of platinum-black to the hammered metal, and that of wood-charcoal to the diamond, or even to coke, may be taken as analogous, in form as well as in chemical action, to that which subsists between the secondary deposit in the cotton fibre, and the comparatively hard and tough pellicle which encloses it.

These observations seem to me to establish two facts: (1.) That cellulose and oxide of iron do not unite chemically; (2.) That in order to be capable of receiving an iron mordant, the cellulose must be furnished with organs or interstices capable of absorbing

that mordant in a state of solution, and minute enough to hold it when precipitated. Neither the mere matter, therefore, of cellulose, nor cellulose presenting only an open surface, is capable of uniting with an iron mordant.

The almost infinite subdivision in the fibre, of the oxide which forms the purple mordant, may be imagined by considering that the solution of iron which produces it contains often not more than $\frac{1}{800}$th of its weight of oxide of iron, and that the cell, therefore, or passage, when filled with that solution, and afterwards dried and changed into sesquioxide cannot (except by one cell robbing another in the act of drying) contain even one-thousandth part of its capacity of the oxide. So minute a proportion of foreign matter cannot be conceived to form an obstruction, even after combination with its colouring matter, to the passage of any solution that may afterwards be applied to the same fabric.

I shall now enumerate a few additional processes which belong to the two different classes, of which I have already given examples.

Class I.—A. The indigo-dye has been already described as the type of those which cotton attracts by its porosity.

B. Bodies, such as safflower, turmeric, &c., which like indigo are colours, *per se*.

C. Bodies which, while they attach themselves to cotton as indigo does, are not, like indigo, possessed of colour, but have the power of attracting and uniting with other bodies, and of forming with them coloured compounds.

a. Tannin is much employed in this way. When cotton is immersed for some time in a warm decoction of gall-nuts, or in a solution of tannic acid, a considerable quantity of tannin is deposited in the fibre; and if cloth so charged be subsequently immersed in the solution of any metal with which tannin is capable of uniting, it is attracted and deposited along with it in the fibre. In this way a black dye is often produced with nitrate of iron. The metallic solution becomes in that case the dyeing material, and the vegetable body the mordant. Tannin attracts also the violet colouring matter of Perkin.

b. Oxide of lead is readily fixed upon cloth on the same principle. The cotton-fibre, by mere immersion in the fluid, separates lead from its solution in lime or in soda, as charcoal does; and when cloth so loaded is treated with a chromic salt, a yellow chro-

mate of lead, or an orange dichromate, is produced. By treating leaded cloth with protosulphate of iron, we obtain, instead of oxide of lead, a deposit of peroxide of iron and sulphate of lead; and if the sulphate by immersion in ammonia be reconverted into oxide, it becomes capable of fixing another equivalent of iron, and so on as often as we alternate the immersions in ammonia and sulphate of iron. It is remarkable that leaded cloth attracts scarcely any iron from the red salts of that metal.

c. Some metallic subsalts give up their excess of oxide in the same manner. Goulard's extract, for example, is almost as suitable for the chrome-orange dye as the plumbite of lime above-mentioned. Sesquichloride of iron, with excess of peroxide, yields but a small portion of its iron to cotton steeped in its cold solution. When heated to near the point at which it becomes turbid, oxide of iron is precipitated abundantly on the cloth, but in a condition no longer capable of attracting a dye. A solution of oxy-chloride of aluminium (Al_2Cl_3, 2 Al_2O_3), of spec. grav. 1·100 deposits a large quantity of alumina on cotton in the cold. It thus forms a mordant for madder and other dyes.

D. Bodies which form mordants for attracting and uniting with other mordants.

a. Tannin fixed in the manner just described is employed to attract tin from an acid solution of tin, and in this way a compound mordant is produced which is the most suitable, by subsequent dyeing in Lima or Brazil wood, for producing what is termed a fancy red, a dye at one time much used as an imitation of Turkey red.

b. As subsalts of iron by themselves do not advantageously deposit their excess of oxide in the cotton fibre when it is immersed in their solutions, the intervention of tin is employed. When cotton is soaked in a cold and weak solution of oxy-chloride of tin, or still better in a mixture of the bichloride and protochloride, and when, after this preparation with tin, it is immersed in oxy-chloride or oxynitrate of iron, a large quantity of iron is deposited in the state, I presume, of a stannate of iron. This mordant, when dyed in ferroprussic acid, forms a Prussian blue of the greatest richness and brilliancy.

Varieties of Class II.—A. The acetate of iron has already been described as an example of this class.

B. Acetate of alumina acts in a similar manner.

C. If we wish to fix upon cloth other oxides, such as copper,

manganese, or chromium, which do not spontaneously part with the acids which dissolve and carry them into the fibre, we must employ an alkali to precipitate them there. The acetate and nitrate of lead being also not spontaneously decomposible, cotton which has been charged with these salts, has to be treated with ammonia or a carbonated alkali, or a sulphuric salt, to fix the lead in the fibre. Aluminated potash is, in the same way, treated with sal-ammoniac; stannate of soda, with weak sulphuric acid; the sulphates and chlorides of manganese and of iron, by caustic soda; the salts of oxide of chromium, by carbonate of soda, &c., &c.

D. Steam-colours, where mordant and dye mix together without combining. The mixture, therefore, retains the solubility of its ingredients, and enters the fibre as readily as either would do in a separate state. Heating in steam of boiling water determines the union and consequent precipitation within the fibre where the mixture had been deposited. Decoctions of those vegetable colouring matters, which form lakes with aluminous salts, are chiefly here referred to.

E. Steam Prussian Blue.—Ferro-prussic acid applied to cotton, and subjected to steam, causes a deposition of white proto-cyanide of iron, which is changed by the air into Prussian blue.

I have thus endeavoured to illustrate two principles on one or other of which dyes can alone enter the cotton fibre. But dyes are not always confined to the interior of the fibre. Previous to the soaping which follows the application of the madder in the madder-purple process, a considerable quantity of the dye remains less firmly fixed than the rest; and in the case of the numerous class of colours which do not require the soaping process, that external dye is allowed to remain. Most colouring matters would not bear so severe a cleansing, and, besides, much richness of hue and velvety aspect would be lost if a portion of them were not left to cover the fibre, and its occasional imperfections. All that class of goods which are dyed with garancine,—the indigo dyes,—all colours fixed by steam, and indeed the great majority of all prints, are in this situation.

We can readily conceive of a tissue so subdivided as the cotton fabric, having passages less perfectly enclosed than those we have been describing, and yet narrow enough to be capable of harbouring more or less securely such insoluble matters as may be left there by an iron or aluminous acetate, during its spontaneous

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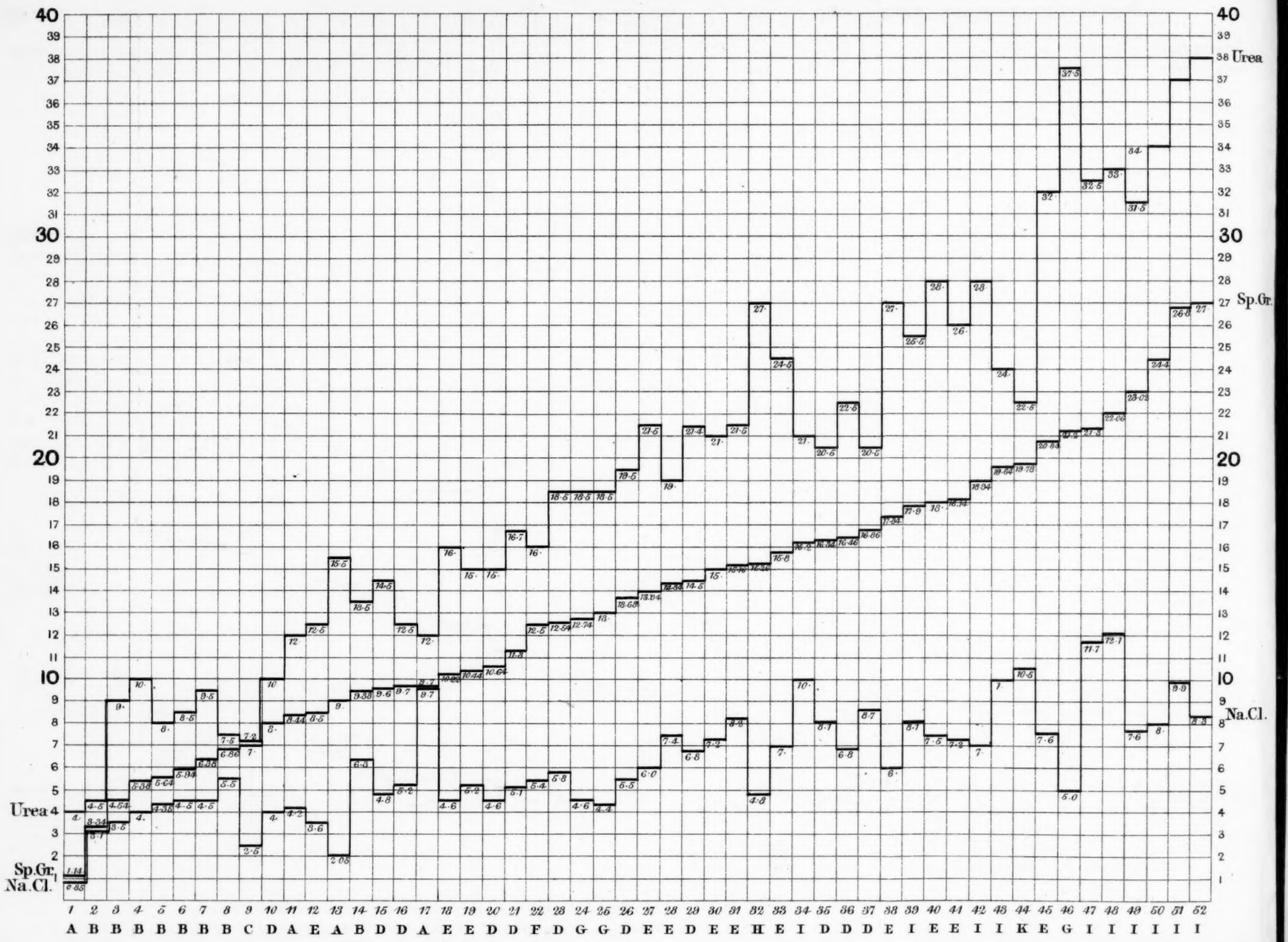


decomposition, and even of exercising to some extent a capillary decomposing power over such a solution as that of indigo. We know, besides, that in many dyes, part of the colouring matter is attached only by cohesion, for which the spaces between the fibres furnish ample opportunity. But all comparatively external adhesions, although of great commercial importance, are only superadditions to the greater amount of dye which is, or ought to be in all cases fixed within the fibre, on one of the two principles which it has been my object to explain.

The "dead cotton" is also apparent in almost all these other dyes; retaining, however, its purity in some more than in others. I have observed it principally in the indigo dye, the chrome-orange dye, the aniline-violet fixed with tannin, and in the dyes from the iron and aluminous mordants where these are attached to the cloth by deposition from basic solutions of their salts. By that method of fixing iron and alumina, white specks appear which would not be discernible when the ordinary mordants are employed. But the "dead cotton" is also distinctly visible (more or less tinged) in all garancine dyes, whether chocolate, black, red, purple, or catechu, even when washing with water is the only means employed to cleanse after dyeing; and it appears in all steam-colours that are well washed.

The dead cotton does not however equally refuse all colouring substances. On examining a safflower-pink dye, the "dead cotton" seems to have attracted its full proportion of it, and the same is the case with the Prussian blue, which is produced from stannate of iron. By repeated dips in the indigo-vat, too, the "dead cotton" is concealed, if not otherwise dyed.

II.—*On the Formation of Organo-metallic Radicles by Substitution.*

By George Bowdler Buckton, F.R.S.

Up to the present time, there appear to be four different methods known for procuring the organo-metallic radicles. These are,

1st. By bringing the reducing action of sunlight to bear upon the haloïd compounds of the alcohol-radicles, in presence of a metal. As an example, the decomposition of iodide of methyl in

presence of mercury, may be quoted. It would appear that iodine is here first set free, which combines with mercury. The nascent methyl also combines with mercury to form mercuric methyl, and, finally, these bodies coalesce into iodide of mercuric methyl, according to the equation,

$$HgI_2 + HgMe_2 = 2\ (HgMeI).*$$

2nd. By the action of potassium and sodium alloys of certain metals, upon the haloïds of the alcohol-radicles. As an illustration, the formation of trimethylarsine may be given.

$$3\ (MeI) + As\begin{cases}Na\\Na\\Na\end{cases} = As\begin{cases}Me\\Me\\Me\end{cases} + 3\ NaI$$

There is also an analogous reaction, representing the formation of a sesqui-ethylated lead-radicle.

$$\begin{matrix}Pb\\Pb\end{matrix}\begin{cases}Na\\Na\\Na\end{cases} + 3\ EtI = \begin{matrix}Pb\\Pb\end{matrix}\begin{cases}Et\\Et\\Et\end{cases} + 3\ NaI$$

3rd. Perhaps the most general method of isolating the organo-metalloïds, is by decomposing the ordinary haloïds of the metals by zinc-methyl, or zinc-ethyl; or by substituting for these haloïds, salts of the organo-metals.

Thus for the first mode :—

$$4\ (PbCl) + 2\left\{\begin{matrix}Zn\ Et\\Zn\ Et\end{matrix}\right\} = \begin{matrix}Pb\\Pb\end{matrix}\begin{cases}Et\\Et\\Et\\Et\end{cases} + 4\ (ZnCl) + 2Pb$$

and for the second mode :—

$$2\ (SnEtI) + \left\{\begin{matrix}ZnEt\\ZnEt\end{matrix}\right\} = \begin{matrix}Sn\\Sn\end{matrix}\begin{cases}Et\\Et\\Et\\Et\end{cases} + 2\ ZnI$$

4th. This method is founded on the displacement of the metal contained in the organo-metalloïd by another metal, which is sup-

* Equivalent of mercury = 200. Corrosive Sublimate $HgCl_2$.

posed to be in a more electro-positive or electro-negative state than that removed. The few experiments I have now to describe, are more particularly connected with this method of operating, and were undertaken, partly with a view to studying the interchange of the true metals contained in various organo-metalloïds, when acted upon by simple metals, or their salts, and partly for testing the action of the metalloïds themselves upon salts of other organo-metallic radicles.

In this manner it was thought some knowledge might be gained, as to how far the conversion of one metalloïd into another might be predicted from our previous acquaintance with the relative electro-positive or negative conditions of the metals employed.

From the well-known reaction represented by the equation

$$3\left\{\begin{matrix}\mathrm{ZnEt}\\ \mathrm{ZnEt}\end{matrix}\right. + 2\,\mathrm{Na} = 2\left\{\begin{matrix}\mathrm{ZnEt}\\ \mathrm{ZnEt}\end{matrix}\right\} + \left\{\begin{matrix}\mathrm{NaEt}\\ \mathrm{NaEt}\end{matrix}\right\} + 2\,\mathrm{Zn}$$

It has been thought that the alcohol-radicles play, in these metalloïds, an electro-negative part towards the respective metals. The extrusion of the zinc in zinc-ethyl, therefore, would be due to its less positive character towards sodium. Many instances occur in which iodine, bromine, &c., may be removed by zinc, sodium, &c., from salts of the organo-metallic radicles, thus affecting their reduction; but the question here proposed for solution was the order of substitution of the metal contained in the radicle by another metal.

From this mode of preparing sodium-ethyl, Mr. Wanklyn surmises that sodium will remove methyl from cacodyl, and take its place, an arsenical alloy being simultaneously formed.

I am not aware that the experiment has been performed, but I have tried a somewhat analogous reaction, triethyl-stibine being employed instead of cacodyl.

Some bright cuttings of sodium were placed in a tube charged with coal-gas, and covered with a few grammes' weight of triethyl-stibine. As no change was observed after three days' contact at ordinary temperatures, the tube was exposed for ten minutes to 160° C. At first, a few bubbles of gas were disengaged from the sodium, and a small quantity of a black deposit was formed, after which all action ceased. A subsequent examination of the contents of the tube, led to the conclusion, that the sodium was unalloyed with antimony, and that triethyl-stibine is, at the above temperature, unattacked by the metal sodium.

If we group together those metals known to combine with the alcohol-radicles, in the following order, which may, in a general manner, be supposed to represent their relative electric positions,

Chlorous or negative elements.	Basylous or positive elements.
O	H
Cl	K Na
Te	Mg
As Sb	Al
Ti Si Bo	Cd Zn
Bi	Hg
Pb	Sn
(Methyl ?)	(Ethyl ?)

we might expect an extrusion of the ethyl from triethyl-stibine even at ordinary temperatures, since that phenomenon is very marked, if mercuric ethyl be employed in place of triethyl-stibine.

Action of Sodium on Mercuric Ethyl.

As this reaction has been elsewhere fully described, I will only here state, that mercury is liberated in the form of a voluminous grey sponge, whilst the sodium-ethyl which is formed, is united in a very unstable condition with mercuric ethyl. This compound is spontaneously inflammable. It explodes violently, and resolves itself into an amalgam of sodium, ethylene, and hydride of ethyl gases.

The formation of the substance appears to be analogous to that of sodium-ethyl, with the difference that mercury is extruded instead of zinc.

The primary action is represented by the equation—

$$3\left\{\begin{matrix}\mathrm{Hg}\,\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Hg}\,\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right. + 2\mathrm{Na} = 2\left\{\begin{matrix}\mathrm{Hg}\,\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right)\mathrm{Na\ Et}\Bigg\} + 2\mathrm{Hg} + \begin{matrix}\mathrm{C_4H_4}\\ \mathrm{C_4H_5H}\end{matrix}$$

If I rightly understand Mr. Wanklyn, he thinks ethyl, &c., should be displaced by mercury, copper, and platinum. The above experiment does not appear to support this idea, since if sodium displaces mercury from mercuric ethyl, it is improbable that mercury would displace sodium from sodium-ethyl.

Bright zinc is not amalgamated when placed in boiling mercuric ethyl. If, however, finely granulated zinc be distilled with iodide of mercuric methyl, appreciable quantities of mercuric methyl pass into the receiver. By far the greater portion of the radicle, however, is split up into gases.

Action of Cadmium on Mercuric Ethyl.

5·6 grammes of mercuric ethyl were digested for some hours with 3·6 grammes of fused chloride of cadmium. The liquid acquired a dark colour, and exhaled a pungent odour, but I failed to isolate any salt of cadmium-ethyl, or the radicle itself.

Zinc-ethyl acts powerfully on fused chloride of cadmium, and forms an unctuous mass, which fumes and finally inflames when exposed to the air.

The cadmium-ethyl remains combined with zinc-ethyl, and is almost entirely destroyed by distillation—a disadvantage also attending its formation from metallic cadmium and iodide of ethyl. This double compound, which seems to adhere to the chloride of zinc, cannot be broken up by solvents. I have attempted to do so with anhydrous ether, bisulphide of carbon, and benzol.

Metallic cadmium does not act on mercuric ethyl.

Action of Bichloride of Tin on Mercuric Ethyl.

These two substances react powerfully, and evolve at the same time great heat. A semifluid mass is formed, from which cold alcohol separates a highly pungent oil, which can be precipitated from the alcohol by water. This proved to be chloride of stannic sesqui-ethyl. The remaining mass of less soluble crystals had all the properties of chloride of mercuric ethyl. The change is represented by the equation—

$$3\left\{\begin{matrix}\mathrm{Hg}\\ \mathrm{Et}\\ \mathrm{Et}\end{matrix}\right\}+\left\{\begin{matrix}\mathrm{Sn}\\ \mathrm{Sn}\end{matrix}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}=3\left\{\begin{matrix}\mathrm{Hg}\\ \mathrm{Cl}\end{matrix}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right\}+\left\{\begin{matrix}\mathrm{Sn}\\ \mathrm{Sn}\end{matrix}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right\}$$

A similar result is obtained if we substitute chloride of stannethyl for bichloride of tin.

$$\left(\begin{matrix}\mathrm{Hg}\\ \mathrm{Et}\\ \mathrm{Et}\end{matrix}\right)+2\left(\begin{matrix}\mathrm{Sn}\\ \mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right)=\left(\begin{matrix}\mathrm{Hg}\\ \mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right)+\left\{\begin{matrix}\mathrm{Sn}\\ \mathrm{Sn}\end{matrix}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right\}$$

Action of Terchloride of Antimony on Mercuric Methyl.

Very considerable heat is produced by the decomposition of these bodies, so much so, as to cause the reduction of a portion of mercury. About one part of terchloride of antimony appears to saturate three parts of mercuric methyl. The resulting mass of crystals, after repeated crystallization from alcohol, gave numbers agreeing with the formula of a double salt:—

$$3(HgMeCl) + SbMe_3Cl_2$$

The reaction with mercuric ethyl is slightly different. Part of the ethyl from the mercuric ethyl passes to the antimony to form triethyl-stibine, which becomes evident by its spontaneous inflammability. Boiling alcohol separates abundance of the crystalline chloride of mercuric ethyl, whilst a considerable quantity of antimony is thrown down by the energy of the action. This reduction is not, however, a necessary condition of the experiment:—

$$3\left(\mathrm{Hg}\begin{matrix}\mathrm{Et}\\\mathrm{Et}\end{matrix}\right) + \left(\mathrm{Sb}\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right. = 3\left(\mathrm{Hg}\begin{matrix}\mathrm{Et}\\\mathrm{Cl}\end{matrix}\right) + \left(\mathrm{Sb}\begin{matrix}\mathrm{Et}\\\mathrm{Et}\\\mathrm{Et}\end{matrix}\right)$$

It is believed that this and the foregoing experiments are, to a certain extent, in accordance with what we might theoretically expect from the relations of the metals to each other. Nevertheless, the reduction appears to be modified in extent, by the presence of the salt resulting from the reaction, and in no case is the reduction complete. We might have anticipated an entire separation of the ethyl from the mercury, perhaps with formation of bichloride of mercury.*

Action of Stannic Diethyl on Metallic Salts, &c.

Stannic diethyl may be boiled for hours with sodium at ordinary pressures, without undergoing change.

Stannic diethyl readily dissolves both iodide and chloride of mercuric ethyl, and again yields them unchanged by evaporation. If the chloride be strongly heated in a sealed tube, mercury is reduced and the pungent chloride of stannic sesquiethyl is formed, with ethylene and hydride of ethyl.

* It is remarkable that bichloride of triethyl-stibine is not attacked by zinc-ethyl, though the biniodide is readily decomposed.

Action of Bichloride of Titanium on Stannic Diethyl.

Mr. Riley having kindly placed at my disposal some pounds weight of rutile, I prepared a quantity of bichloride of titanium, by passing chlorine at a low red heat over pellets made of a paste of powdered rutile, lamp-black, and a little gum.

The first crude product is often contaminated with sesquichloride of iron, but by distillation this may be readily removed, and what passes into the receiver is nearly pure.

Stannic diethyl mixes freely with the fuming bichloride of titanium, but no reaction commences until the liquids are heated, when there is an abundant evolution of gas. At the close of the experiment, a tenacious purple mass is obtained. On agitation with water, a heavy stratum separates from a fine purple aqueous solution, which last, when decanted and treated with dilute potash, precipitates a non-combustible purplish-violet body. This substance rapidly becomes white in the filter, absorbs oxygen, and is converted into titanic acid. The aqueous solution is therefore nothing but sesquichloride of titanium, described by Rose and others.

An examination of the lower stratum, which is terribly pungent, proved it to be chloride of stannic sesquiethyl. Taking the evolution of gas into consideration, the change is represented by the equation—

$$\begin{matrix}\mathrm{Sn}\,\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Sn}\,\mathrm{Et}\\ \mathrm{Et}\end{matrix} + 2\left\{\begin{matrix}\mathrm{Ti}\,\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Ti}\,\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. = 2\left\{\begin{matrix}\mathrm{Ti}\,\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Ti}\,\mathrm{Cl}\end{matrix}\right. + \begin{matrix}\mathrm{Sn}\,\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Sn}\,\mathrm{Et}\\ \mathrm{Cl}\end{matrix} + \mathrm{C_4H_5Cl}$$

My own experience coincides with that of M. Cahours, that salts of titanium do not furnish titanic ethyl when distilled with zinc-ethyl. The reaction is very violent, but difficulties interpose similar to those noticed in the preparation of cadmium-ethyl. There are good reasons for supposing, however, that, as soon as titanic ether has been prepared, titanic ethyl may be obtained from it, through the instrumentality of zinc ethyl.*

* I have not been fortunate in obtaining titanic ether by distilling together titanate of potassium and sulphovinate of potassium. Chloride of titanium yields with sulphovinate of potassium, a distillate, boiling at 92°, composed of mixed alcohol, hydrochloric acid, and chloride of ethyl. Sulphates of titanium and potassium remain in the retort.

This reaction would be analogous to that lately made known by Dr. Frankland, in the preparation of boric ethide and boric methide;—a reaction very interesting, since it tends to show that oxygen as well as chlorine is, in certain instances, capable of substitution by ethyl.* I may mention, also, that plumbic acid, Pb_2O_4 powerfully acts on zinc ethyl with reduction of the lead. I have not taken the necessary steps, by this means, to isolate plumbic ethyl, but I think it highly probable that under reduced atmospheric pressure, the radical may be thus procured by distillation.

Titanium in its properties is, perhaps, more nearly allied to silicon than to tin, and considerable difficulty has been hitherto found in combining silicon with ethyl. It can scarcely be doubted that these bodies exist, and may hereafter show themselves through some well devised reaction.

A resinous mass is obtained by acting on mercuric ethyl with bichloride of titanium, and much chloride of mercuric ethyl is produced.

If we reason analogically from the tin reactions with mercuric ethyl, we should expect chloride of titanic sesquiethyl to be formed. I cannot yet confidently answer the question whether this body, or more simply the sesquichloride of titanium, is one of the products of the decomposition.

It is still a question of considerable interest how far, and in what manner, the introduction of different metals can be effected in organo-radicles represented by the type—

$$\left.\begin{matrix} R \\ R \end{matrix}\right\} \begin{matrix} X+ \\ X+ \\ X+ \\ X+ \end{matrix}$$

Can RR be represented by two different metals, in the same manner as X may represent different alcohol-radicles? It has been seen, that the result of the direct union of stannic diethyl with chloride of mercuric ethyl has not affirmatively answered the question as to the existence of chloride of mercuro-stannic sesquiethyl.

It is thought that the foregoing experiments, in their simpler forms, show that the metallic substitutions are pretty nearly those

* M. Wurtz is inclined to think that, as ethyl has many analogies with chlorine, it may also take the place of peroxide of hydrogen; and he thinks this, in reality, happens in the formation of boric ethide.

indicated by their electro-position, but that the results are modified by the more or less saturated condition of the metals contained in the radicles.

Dr. Frankland observes, that the atomic powers of an organic radicle have reference to its stages of stability, dependent upon its points of saturation, and Dr. Hofmann expresses much the same, in stating that the basic properties of bodies intensify with the increase of their assimilated electro-positive alcohol-radicles.

The complete saturated condition of a body does not of necessity represent its most stable form. The sesquiethylated compounds of lead and tin are the most stable salts of those radicles, being capable, in some cases, of being distilled from aqueous caustic potash. Triethyl-stibine is more stable that either tetrethyl- or pentethyl-stibine, and the same remark holds with respect to the ordinary chlorides of antimony.

It has been further shown, that the mercuric organo-metals may be partially, or entirely reduced by tin-compounds, and that stannic diethyl reduces bichloride of titanium to sesquichloride, ethyl being given up for chlorine.

I must express a hope that some of the missing numbers of this interesting and important group of substances will, through similar treatment, discover themselves to the chemist.

III.—*On the Specific Gravity of Urine as a Measure of its Solid Constituents.*

By Edward Nicholson, F.C.S., Staff Assistant-Surgeon.

Rules have been given to find, from the specific gravity of human urine, the quantity of solids or of urea which it contains. Dr. Golding Bird's rule for ascertaining the solids of the urine was to multiply the excess of specific gravity over that of water by 2·33; and Mr. Haughton, in his valuable investigations, "On the Constants of the Human Urine," states that the quantity of urea bears a very simple relation to the specific gravity. But some experiments I have been making on the subject are far from confirming these results; and when the sources of the urinary constituents are considered, it will be seen that such a simple ratio between the specific gravity and the urea would be very un-

likely to occur. If the solids of the urine were solely the result of tissue-metamorphosis, and the mutual proportions of the different constituents were constant, these rules would be perfectly applicable. But the solids of the urine are not solely the result of tissue-metamorphosis, but also of many accidental circumstances; and the mutual proportions of many of the constituents are far from constant. The sulphuric acid of urine being nearly all derived from the disintegration of nitrogenised tissue, its quantity is in very constant proportion to the urea, while phosphoric acid, being mainly produced by the disintegration of the organs of the nervous system, is often independent of the urea. I have seen the phosphoric acid fall to less than one-tenth of its normal proportion to the urea, while the sulphuric acid remained as usual in constant proportion. Another disturbing element is the chloride of sodium. This salt follows no law in its proportion in the urine, and its erratic course affects most considerably the specific gravity.

The line given by Mr. Haughton as representing the urea in urine of gradually increasing specific gravity, was of a very trifling curve; it formed the arc of a large circle, cutting the specific gravity-line in two points, but for practical purposes corresponding to it very closely. It will be seen in the following table and in the diagram, that the ratio of the specific gravity to the urea is totally irregular, and that none of the rules given would give the smallest approximation to the amount of urea; and this is true whether the urine of one individual or of several be taken, and whether the subjects be in health or in disease. As I had long been in hopes that some simple ratio existed between the urea and the specific gravity, I took especial care, in the analyses I performed, to note with accuracy the specific gravity of the urine. To this effect, all the determinations of specific gravity were made by the balance: for I find that urinometers, even of the best construction, give an error amounting often to ·002. The fifty-two specimens of urine given in the Table form the totality of my analyses, in which urea and chloride of sodium were determined; many other analyses (made for pathological inquiry), in which only one or other of these substances was determined, have been rejected. Owing to the occurrence of several cases under my care, in which the specific gravity was very low, I am enabled to show a considerable range of specific gravities. The individuals, whose urine has been analysed, were ten in number, two of whom were

healthy adults, the others were patients in the General Hospital, Fort Pitt.

I will distinguish them as follows:—

A.	Disease—Intermittent fever.....	4	observations.
B.	do. Chronic dysentery.....	8	do.
C.	do. Anæmia	1	do.
D.	do. Enlarged liver	11	do.
E.	do. Enlarged spleen.....	12	do.
F.	do. Paralysis.....	1	do.
G.	do. Albuminuria (slight)....	3	do.
H.	do. do.	1	do.
I.	Healthy.....	10	do.
K.	do.	1	do.
		52	

	Specific gravity.	NaCl per 1,000.	Urea per 1,000.		Specific gravity.	NaCl per 1,000.	Urea per 1,000.
1. A	1001·14	·85	4·	27. E	1013·94	6·	21·5
2. B	1003·34	3·1	4·5	28. E	1014·34	7·4	19·
3. B	1004·54	3·5	9·	29. D	1014·5	6 8	21·4
4. B	1005·38	4·	10·	30. E	1015·	7·2	21·
5. B	1005·64	4·35	8·	31. E	1015·16	8·2	21·5
6. B	1005·94	4·5	8·5	32. H	1015 26	4·8	27·
7. B	1006·38	4·5	9·5	33. E	1015·8	7·	24·5
8. B	1006·86	5·5	7·5	34. I	1016·2	10·	21·
9. C	1007·	2·5	7·2	35. D	1016·34	8·1	20·5
10. D	1008·	4·	10·	36. D	1016·46	6·8	22·5
11. A	1008·44	4·2	12·	37. D	1016·86	8·7	20·5
12. E	1008·5	3·6	12·5	38. E	1017·34	6·	27·
13. A	1009·	2·05	15·5	39. I	1017·9	8·1	25·5
14. B	1009·38	6·3	13·5	40. E	1018·	7·5	28·
15. D	1009·6	4·8	14·5	41. E	1018·14	7·2	26·
16. D	1009·7	5·2	12·5	42. I	1018 94	7·	28·
17. A	1009 7	9 7	12·	43. I	1019 64	10·	24·
18. E	1010·22	4·6	16·	44. K	1019 78	10 5	22·5
19. E	1010 44	5 2	15·	45. E	1020·84	7·6	32·
20. D	1010·64	4·6	15·	46. G	1021·2	5·	37·5
21. D	1011·3	5·1	16·7	47. I	1021 3	11·7	32 5
22. F	1012·5	5·4	16·	48. I	1022·06	12·1	33·
23. D	1012 54	5·8	18·5	49. I	1023·02	7·6	31·5
24. G	1012·74	4·6	18·5	50. I	1024·4	8·	34·
25. G	1013·	4·4	18·5	51. I	1026·8	9·9	37·
26. D	1013·68	5·5	19.5	52. I	1027·	8·3	38·

The influence of chloride of sodium over the ratio of urea to specific gravity cannot fail to be remarked. In the specimens of equal specific gravity, a slight variation in the quantity of chloride

of sodium is accompanied by a considerable fluctuation of urea in the inverse direction. The great influence which chloride of sodium thus possesses over urea is explained by the fact, that, whereas a solution of chloride of sodium of sp. gr. 1010 contains 14 per 1000 of the salt, a solution of urea of the same specific gravity contains 35·6 parts per 1000. This fluctuation, as exemplified in the series 27 to 34, is often very regular, and in many cases it is sufficient to add to the specific gravity the difference between it and the chloride of sodium, to obtain the urea within 5 per cent. of error; but in many cases the error may amount to as much as 20 per cent., the amount obtained being below the real number in dilute urines, above it in concentrated specimens.

It is evident from these results that determining the specific gravity only of the urine is of no good for calculating the amount, either of urea or of solids excreted; but that, by taking into consideration the amount of chloride of sodium (which can be determined in two or three minutes by a standard solution of nitrate of silver), the quantity of urea may, within certain limits, be calculated for clinical purposes. However the necessity of an accurate determination of specific gravity renders it far more advisable to put aside all inexact methods, and proceed at once to the volumetrical estimation of urea.

IV.—*On the Solvent Power exercised by a Solution of Hyposulphite of Soda upon many Salts Insoluble in Water.*

By Frederick Field, F.R.S.E.

In a paper published in the Chemical News (vol. 2nd) upon the reaction of hyposulphite of soda on the chloride, bromide, and iodide of silver, various experiments were cited to prove the comparative insolubility of the latter compound in very weak solutions of the hyposulphite; the addition of a small quantity of iodide of potassium to a solution of chloride of silver in hyposulphite of soda causing an immediate precipitate, even when very small quantities of metal are present.

My attention has subsequently been directed to the solvent

power of hyposulphite of soda upon many other salts which are perfectly insoluble in water.

Sulphate of Lead.—This compound is dissolved to a very considerable extent in the alkaline hyposulphite. When solutions of the sulphate and hyposulphite of soda are mixed, and nitrate of lead added, no precipitate takes place; or if sulphate of lead be previously formed and digested in a solution of hyposulphite of soda, it is dissolved. Even the native crystallised sulphate enters into solution after some little time, and a few minutes' digestion with the soda-salt is sufficient to obtain abundant evidence of lead in solution. On heating the liquid, the metal is precipitated as sulphide.

As the chromate of lead appears to be insoluble in the hyposulphite, it was hoped that the separation from the sulphate might be effected by this means, which would facilitate to a very great extent the determination of chromium in chromate of iron, when bisulphate of potash is employed for the decomposition of that mineral; the results, however, were not altogether satisfactory, as the chromate of lead is partially decomposed, and an alkaline chromate passes into solution.

Iodide of Lead is instantaneously dissolved, and apparently, to almost any extent, in hyposulphite of soda, forming a colourless solution.

Hydrated Protoxide of Copper is gradually dissolved—the solution becoming nearly colourless. On heating, an orange powder (the suboxide) is precipitated, but is eventually converted into the sulphide.

Hydrated Suboxide of Copper is very freely dissolved in the cold, but is partially precipitated when the solution is warmed.

Red Iodide of Mercury is excessively soluble in the hyposulphite of soda. When the colourless solution is cautiously heated, a dull red powder is gradually deposited, which was at first mistaken for a mixture of the iodide and sulphide. On examining the product, however, it was found to be perfectly free from iodine—the precipitate consisting of the red modification of sulphide of mercury.

Sulphate of Lime is far more soluble in a solution of hyposulphite of soda than in water, one fluid ounce of the former, not particularly strong, dissolving rather more then four grains of the lime-salt. The introduction of a small quantity of the hyposulphite into the waters used in boilers, &c., which contain

sulphate of lime, might possibly prove advantageous by preventing incrustation.

Oxalate and carbonate of lime, carbonate of lead, and the sulphates of baryta and strontia, appear to be quite insoluble in solution of hyposulphite of soda.

V.—*Notes on certain Processes of Rock Formation now in Action.*

By Arthur H. Church, B.A.

In the summer of 1860, my attention was directed to an interesting phenomenon occurring on the east side of Bude Haven, Cornwall. The beach is composed almost wholly of the débris of the shales, &c., which partly form the cliffs, mingled however with numerous fragments of recent sea-shells. This coarse-grained sand (of which large quantities are annually removed for agricultural purposes), is in some places becoming slowly consolidated into a sort of conglomerate, by the action upon it of the water of land-springs. Such a formation has evidently been going on at various points in the neighbourhood for many years, and, in fact, absolutely identical rocks so formed are now in their turn being worn away by the destructive agency of the sea.

I accounted for the consolidation of the sand by the natural supposition that the fresh water falling into it contained excess of carbonate of calcium held in solution by free carbonic acid, which, when it escaped by exposure to the air, allowed the carbonate of calcium to be deposited between the sandy particles as a cementing material. But I found that, in several cases at least, the water was by no means particularly hard, although, in one place where the consolidation was proceeding rapidly, I observed that the leaves of the plants growing in the interstices of the rock over which the water trickled, were quickly incrusted while living with small specks and discs of carbonate of calcium, deposited by the falling waters. These discs, by thickening and extending, soon formed a complete envelope to the leaf, and arrested further development.

A rough analysis of the consolidated sand taken from below the rock above-named, revealed to me at once that it contained

on an average 5 per cent. more carbonate of calcium than the loose sand, of which silica and alumina formed by far the larger portion. But, on the other hand, some specimens of consolidated sand from neighbouring localities actually contained less carbonate of calcium than the loose sand lying near them. These specimens were from spots where the land springs did not make any marked deposit or incrustation. One chemical difference was however noted with regard to them: they contained but a mere trace of chloride of sodium, instead of the abundant proportions found in the porous particles of the sand itself. Here, I think, lies the explanation of the result. The water of the land-springs, charged with carbonic acid, though not containing a great surplus of earthy matters, removes from the sand on which it falls, and through which it percolates, a portion of its carbonate of calcium and of its marine salts. Some of the former substance is slowly deposited from solution as a cementing material, owing to the gradual escape of carbonic acid, while the chloride of sodium and other salts, being permanently soluble, filter away almost completely. The phenomenon seems, therefore, to be generally due to a re-arrangement of some of the constituents of the sand, rather than to any addition which the fall of fresh water into it might make. This hypothesis affords a means of explaining many remarkable recent formations, and it closely resembles in its principle the theory on which I accounted for the formation and composition of the interesting mineral, Beekite (Phil. Mag., Feb., 1862; Journ. Chem. Soc., June, 1862). In that case it was assumed that water charged with carbonic acid and silica removed the carbonate of calcium from corals, shells, &c., and deposited silica in its room, a portion of the calcium compound also being re-arranged and reprecipitated.

Mr. S. P. Woodward, in the November number of the Intellectual Observer (pp. 280—284) gives an interesting note concerning the fossil human skeleton from Guadaloupe, now in the British Museum. That the fossilization of this and many other old-looking specimens may have occurred in quite modern times, is abundantly shown by the rapid rate at which deposits of travertine and similar substances, take place under the most varied conditions, and in very numerous localities. In the instance of the Guadaloupe skeleton, it would appear that the solidification of the surrounding loose coral-sand progressed gradually, forming a concretionary mass around the bones; also, that from these struc-

tures, a displacement of phosphate of calcium had occurred in the way to which I have before alluded.

The chemical conditions under which the vast geological changes continually taking place are effected, deserve more careful investigation. The study of these changes, especially so far as they concern the recent formation of rocks, must throw light on many difficult historical problems, such as those relating to the succession of life upon the earth, and to the former existence of animals and plants in strata where all traces of organic forms have been destroyed. For example:—The transposition of certain mineral compounds proper to organic structures into the rocky matrix in which such fossil structures lie, and in which these particular mineral compounds do not otherwise occur, frequently points almost with certainty, to the agency of water; this conclusion probably involving and explaining, in its turn, other local appearances.

I have mentioned the rapidity with which deposits of travertine take place in many localities, and details relating to numerous instances of this action have been recorded. Sometimes the deposit overtakes the growth of a moss, and actually arrests further increase, by enclosing the whole plant in a stony envelope. I noticed an instance near Bude, where a thick crust of carbonate of calcium had formed upon a frond of the fern, *Scolopendrium vulgare*, and had prevented the full development and ripening of its spores. In the course of ten days, this frond, which, when I first observed it, was but half covered with circular patches of the earthy deposit, had become completely coated. The circular patches were at first loosely adherent to the frond, and when removed, generally disclosed a brown discoloration of the vegetable structure beneath. Further evidence of decay was found in the presence of humous bodies, and of crenic acid in the incrustation itself. That these, and other ill-defined products of the destruction of vegetable tissues, often occur in large proportion in calcareous deposits, was strikingly shown by one specimen which I obtained from the neighbourhood of that great mass of travertine known as Southstone Rock, in the valley of the Teme, Worcestershire. This specimen was perfectly homogeneous, and contained no vegetable remains, yet when heated it blackened, and finally burnt, after the manner of peat. On analysis it was found to contain, besides carbonate of calcium, oxides of iron and manganese, and other mineral constituents, no less than 13·7 per cent. of organic

matter. This fact seems to be of some importance in connection with the origin and formation, in certain older rocks, of such fossil carbonaceous substances, as retinite, bitumen, elaterite, and petroleum.

But carbonate of calcium is not the only material which serves as a cement in consolidating sand and débris, or which constitutes a rocky deposit. In the ochre-pit on Shotover Hill, near Oxford, numerous geodes of iron-ore occur, each containing a nucleus of ochre or clay; such nodules are also found in great abundance in many other localities. The interior part of the shell of these geodes consist of magnetic oxide and of hydrated sesquioxide of iron. Exterior to this is an envelope of sand-grains, agglutinated by means of the hydrated sesquioxide. As the chalybeate water of the pit still percolates through the sand, the continuance of the consolidating process may be watched in the notable increase in size of the sandy covering of particular nodules. Again, in the same neighbourhood, in a field above Bullingdon Marsh, a formation of magnesian limestone is now going on, the deposit, in this case, covering and cementing together leaves, stems, and other vegetable fragments. The proportion of magnesium-salt in this deposit is, in some specimens at all events, sufficiently large to have induced attempts to separate it on a scale of commercial importance.

From the consideration of the various phenomena to which I have alluded, and of many others similar to them, I think we are justified in concluding that water acts as a rock-former, not only by its power of adding fresh materials, but also in virtue of its various functions as a re-arranger of the old. This view is borne out by the numerous instances where those constituents of a stratum which exist in but small proportion to its chief ingredient, gradually separate out from the mass. Illustrative examples are found in the silicified concretions about organic nuclei,* occurring in the chalk, viz.: flints, pot-stones, &c.; and also in such minerals as allophane and collyrite, rich in silica and alumina, also found in fissures of the chalk; while, on the other hand, where, as in clay, silica and alumina preponderate, there nodules rich in carbonate of calcium are found.† The septaria from the London

* The intestine movements of the decomposing organic molecules appear to have determined the action.

† The author exhibited specimens of all the minerals, &c., referred to: among them a remarkably regular calcareous nodule, from Jordan-hill N.B., and others from London clay (in the Regent's Park).

clay, with their crystallisations of sulphate of calcium, may also be here alluded to; yet the simple agency of water is scarcely sufficient to account for the large crystals of sulphate of barium, which also occur in these concretions (and in some stalactites), and for many veins of metal and insoluble metallic sulphides. However, it is possible, that in some instances, the substance found is not that first formed. If organic matter and sulphate of barium are both in contact with water, we may reasonably suppose that a portion of the barium might enter into solution as *sulphide*, and that this compound, on exposure to the atmosphere, might again recover its lost oxygen, and resume the insoluble state. An excellent example of such a conversion is found in pyritified wood, &c.; a piece of wood, saturated with protosulphate of iron soon becomes filled with innumerable crystals of insoluble sulphide of iron; and these again, on exposure to air and moisture, are reconverted into the original soluble salt.

I have preferred to give my general conclusions rather than to tabulate my numerous but somewhat discordant analyses; the Society will also, I trust, excuse the imperfection of these notes, which are intended merely to direct attention to a few connected phenomena of some interest.

VI.—*On the Composition of Gallstones.*

By J. L. W. Thudichum, M.D.

(Second Communication.)

Water-extract of Ox-Gallstones.—Diluted with water, and treated with dilute sulphuric acid, it immediately deposited a soft resin of a brown colour. This was collected and removed in a lump from the fluid. The acid solution continued to be turbid, and was therefore heated for some time, and then filtered; but the suspended matter passed through the filter. After weeks of standing, the precipitated matter had collected at the bottom, and the dark brown fluid was clear. It was removed by decantation, and the deposit was collected. The

three parts, namely, the first resinous, and the second, or flocculent precipitate, and the acid mother-liquor were further treated as follows:

Resinous Precipitate.—It was washed with water by kneading with a pestle in a mortar, and then dissolved in hot concentrated alcohol. The solution hardly deposited anything on cooling and standing, and on the addition of small quantities of ether. To the solution, baryta-water was added, and although at first no precipitate was perceptible, a deposit ensued when the solution was concentrated.

This deposit was collected on a filter, washed with water, and then boiled with absolute alcohol. Scarcely anything dissolved in this agent. The deposit was then decomposed with hydrochloric acid, which caused slight effervescence, owing to the presence of some carbonate of baryta. The residue was washed with water, boiled with alcohol, and thrown on a filter. The filtrate on cooling deposited needle-shaped crystals, grouped in balls and blended masses; they were fusible by heat, and perfectly combustible on platinum foil. The insolubility of the baryta-salt in water and boiling alcohol, and the solubility of the acid in boiling alcohol, and its crystallisation in needles, characterise it as *cholonic acid.*

The solution from which the cholonate of baryta had been deposited contained a considerable amount of a brown baryta-salt, which was soluble in water and alcohol, not crystallisable, and appeared to be *glycocholate of baryta.*

The flocculent deposit was dissolved in alcohol, and after this solvent had again been evaporated, remained as a resinous matter. Potassa combined with this resin, formed a solution in which an excess of potassa formed a precipitate. The excess of potassa containing a little matter in solution, being removed by decantation, the precipitate readily dissolved in water. From this solution a resin was precipitated by chloride of ammonium. This resin consequently was *cholonic acid.*

The *fluid* from which the biliary acids had been precipitated by sulphuric acid, was distilled; the distillate had a very bad smell and contained hydrochloric acid, but scarcely anything organic. The fluid in the retort deposited some dark resin during the boiling. It was treated with carbonate of baryta and baryta-water to remove sulphuric acid. The brown alkaline filtrate was again distilled, and the distillate evaporated with some hydrochloric acid.

A small quantity of a crystalline chloride of a strongly smelling, probably compound *ammoniacal base* remained. The fluid in the retort, after further concentration in a china dish (further distillation having become impossible by the frothing of the mass), deposited crystals of *carbonate of soda.*

The water-extract of ox-gallstones yielded therefore the following ingredients:—

Phosphate of lime.
Glycocholate } of Soda.
Cholonate }
Salt of resinous acid related to the foregoing.
Hydrochlorate of soda.
Ammoniacal base.
A matter having a very repulsive odour.
A syrupy brown mother-liquor.

Hydrochloric Acid Extract of Ox-gallstones.

When this extract was repeatedly evaporated to dryness, it deposited a dark brown precipitate, which consisted of *cholochrome* and some inorganic matter, which on incineration was left as a white fixed *residue.* The ingredients of this residue will be stated lower down. The extract at last was a thick acid syrup, in which on standing, some uncertain crystallisation ensued. Mixed with water, it formed a dark brown solution, which smelt like an old bottle of pickled onions, and coloured black the inside of a stoppered bottle made of glass containing lead. Both the smell and the formation of sulphide of lead point to the presence of a *sulphur compound,* which had not been entirely destroyed by the boiling with hydrochloric acid (which, it will be remembered, had caused the evolution of some sulphuretted gas). The dilute extract exhibited moreover the following reactions:—

It was acid to test paper.

Ferrocyanide of potassium produced a copious white precipitate, which was only partially dissolved by hydrochloric acid, and speedily became blue. The blue colour which the solution at first assumed, was due to the presence in it of a *trace of iron.* The increase of the blue colour had to be ascribed to the decomposition which the ferrocyanide always experiences in this reaction (as will be seen, with *zinc,* in the presence of a trace of iron). This

white precipitate was not dissolved by the addition of nitric acid, but on heating, solution ensued with slight effervescence.

A little of the solution was mixed with an equal bulk of hydrochloric acid, and ferrocyanide was then added. The bluish-white precipitate was quickly produced.

Ferricyanide of potassium produced a yellowish-red precipitate, of which a part was soluble in hydrochloric acid, denoting the presence of *zinc* and a *trace of copper*.

Ammonia precipitated a colourless matter, partly soluble in an excess of the reagent.

Sulphide of ammonium produced a copious grey precipitate.

The dilute acid extract was now treated with sulphuretted hydrogen, until, after violent shaking, it smelled strongly of the gas. A copious grey precipitate fell down. This, after purification, was digested for an hour with warm sulphide of ammonium, but although after filtration, the solution from yellow had become brownish red, it extracted no metal from the precipitate, which was still grey. A part of it, dried and ignited on platinum, left a a white residue, not easily soluble in hydrochloric acid, easily soluble in aqua regia; the solution was not precipitated by water, but by ammonia, an excess of which dissolved the deposit entirely. The precipitate having thus been shown to consist of sulphide of zinc only (with the merest trace of iron, to which it owed its grey colour) was heated in a platinum vessel, redissolved in hydrochloric acid with the addition of a little nitric acid; and the solution was mixed with water, heated to ebullition, and treated with excess of carbonate of soda, when white *basic carbonate of zinc* fell down as a copious precipitate.

The precipitation of zinc from the acid extract by means of sulphuretted hydrogen made it probable that there was contained in the extract, a fixed organic acid, capable of driving out the the hydrochloric on evaporation, but having itself only so weak an affinity for zinc in acid solution, as to yield it in part at least to sulphuretted hydrogen, similar to acetic, lactic, and leucic acids. To isolate such a body, the concentrated extract was shaken with repeated portions of ether. The ether was separated, and after distillation left a fluid, which became turbid on cooling, and had a strong acid reaction; the ether also had an acid reaction after distillation, and the flask in which the distillation had been performed contained a vapour which coloured blue litmus paper red, and gave a white precipitate with silver-solution, and was there-

fore hydrochloric acid. The ethereal extract, evaporated on the water-bath, left a yellowish granular matter, which under the microscope also appeared as amorphous granules. It was easily soluble in water, particularly when hot, little soluble in alcohol. It burned with a bluish flame, giving out a smell like that of burnt horn and somewhat aromatic, lastly a cyanic vapour, and left a bulky charcoal, which though difficult to burn, left no residue of a mineral nature.

The liquid from which organic matter had been extracted by ether, and which contained all that sulphuretted hydrogen had not precipitated, was saturated with ammonia and treated with sulphide of ammonium. The precipitate, at first gelatinous and colourless, became green under the influence of the sulphide. It was filtered; the filtrate was greenish yellow. The green precipitate during washing became quite white by oxidation of a trace of iron, and the filtrate of a much paler colour. The deposit was dissolved in hydrochloric acid, and digested for some time, a little nitric acid being added. The solution was neutralised with carbonate of soda, and a slight excess of alkali added; acetic acid was then added to the mixture in excess, when a very slight precipitate of *phosphate of iron* remained. To the filtrate chloride of iron was added until a filtered portion produced a blue stain on paper moistened with ferrocyanide of potassium. The bulky precipitate of white *phosphate of iron*, which did not change colour on heating, was filtered off. The filtrate was treated with a great excess of ammonia, which precipitated all the iron that had been added in excess. The filtrate from the oxide of iron gave a *precipitate* when treated with sulphide of ammonium, which was yellowish, and when heated on platinum, decomposed, leaving a gray mass, which did not become white after long exposure to red heat. Treated with nitric acid, it effervesced, dissolved, and on evaporation and heating, left a fusible mass. This gradually dried up, and ultimately left a reddish matter. This was easily soluble in hydrochloric acid, and after heating, formed a colourless solution. After slow evaporation, and the removal of all excess of of acid, it became a white residue, which, after solution in hot water and cooling, shot into a mass of fine needles: of these, when separated, a part remained soluble in hot water, another could only be dissolved again by the addition of a trace of acid. In this solution, sulphide of ammonium produced a precipitate, which after washing, was flesh-coloured. A portion heated with peroxide

of lead and excess of nitric acid, produced a beautiful red solution. The precipitate consisted consequently of sulphide of manganese.

To the filtrate, which was now free from all substances that could be precipitated by sulphide of ammonium and caustic ammonia, and had been heated to boiling, carbonate of ammonia, chloride of ammonium and caustic ammonia were added. A copious white precipitate of *carbonate of lime* fell down. This was the lime which in the gallstones had been combined with *phosphoric acid.* The filtrate from the lime was treated with phosphate of soda and ammonia; no immediate precipitate ensued. On standing the fluid remained quite clear, thus showing that no magnesia, in combination with phosphoric acid, had been precipitated by the sulphide of ammonium.

The filtrate from the first sulphide of ammonium precipitate, which, as mentioned, was greenish yellow, was heated to ebullition, and chloride of ammonium, ammonia, and carbonate of ammonia were added. A bulky white precipitate of *carbonate of lime* ensued, containing the lime which in the gallstones had *not* been in combination with phosphoric acid. To the filtrate phosphate of soda and excess of ammonia was given. After twelve hours a deposit of crystals of phosphate of ammonia and *magnesia* had formed. This deposit was but a moderate percentage of the quantity of lime. The magnesia contained in it must be assumed not to have been in combination with phosphoric acid.

First portion of Matter deposited by Hydrochloric Acid extract on Evaporation.—It was dark-brown, nearly black. When washed and dried it became very brittle. Heated in a platinum crucible it emitted vapours, resembling in smell those of impure tyrosine; it then took fire, emitting the smell of cyanogen, and was ultimately consumed, leaving a bulky ash of the shape of the original lumps of matter.

This residue was powdered and heated once more, in order to consume a remnant of carbonaceous matter. It was treated with hydrochloric acid. The greater part dissolved, but a small amount of black matter remained undissolved.

This latter black residue, on heating, became white, with a shade of rose-colour; extracted with hydrochloric acid, it yielded up some oxide of iron, and then remained white after exposure to red heat. It assumed a blue colour, when heat was applied, after a solution of cobalt had been brought in contact with it, and dis-

solved in caustic potassa; this solution, neutralised with hydrochloric acid, and made alkaline with ammonia, gave a white precipitate. The substance was, therefore, *alumina*.

The acid solution was found to contain the greater part of the iron which had been present in the gallstones. It was treated with ammonia and sulphide of ammonium, which produced a black deposit. This, after filtration and washing, was dissolved in dilute warm hydrochloric acid. (A trace of residue on the filter, treated with concentrated nitric acid and excess of ammonia, exhibited a trace of *copper*.) The solution was digested with a little nitric acid. It was then made alkaline with carbonate of soda, a precipitate forming, and again acidified with acetic acid, part of the white precipitate remaining undissolved. This, from the nature of the proceeding, could be nothing but *phosphate of iron*. The solution, which before had been strongly yellow, now, after removal of the precipitate by filtration, was perfectly colourless. Chloride of iron was now added, and the mixture was heated. A copious precipitate ensued, which became brownish. When the solution, after filtration, gave a blue stain upon paper moistened with ferrocyanide of potassium, all *phosphoric acid* was precipitated in combination with iron. The precipitate was separated by filtration. To the clear filtrate oxalic acid was added, when a copious white precipitate ensued. This was collected in the usual manner. It contained the *lime*.

To the filtrate from the oxalate, chloride of ammonium, excess of ammonia and phosphate of soda were added. The sides of the glass were rubbed with the glass rod. After some hours a very slight crystalline precipitate of ammonio-phosphate of *magnesia* had formed.

Second portion of Matter deposited from Hydrochloric Acid extract on Evaporation.—It was collected, washed, and heated to redness. The residue dissolved in hydrochloric acid, yielding a brown solution. Sulphuretted hydrogen caused a slight deposit, which contained no copper, and could not be defined any closer. The acid solution was next treated with sulphide of ammonium. The precipitate, coloured green by iron, was, after washing, dissolved in warm dilute hydrochloric acid, and mixed with the solution of the sulphide of ammonium-precipitate from the last syrup of the extract. The alkaline filtrate was mixed with the alkaline filtrate of the last extract, and analysed in the manner already described.

The first portion of deposit from the hydrochloric acid extract contained :—

Cholochrome (probably combined with iron, alumina, and lime).
Oxide of iron.
Alumina.
Copper (a trace).
Phosphate of iron.
Phosphoric acid.
Lime.
Magnesia.

The second portion of deposit contained :—

Cholochrome.
Iron.
Phosphate of lime and magnesia.

The remaining extract, after repeated evaporation to dryness, and dispersion of all free hydrochloric acid, contained in solution :—

Zinc.
Cholochrome (little).
A new organic body (soluble in ether).
Phosphate of iron.
Phosphoric acid.
Manganese.
Lime (combined with phosphoric acid).
Lime (combined probably with cholochrome).
Magnesia (combined probably with cholochrome.)
Ammonium (chloride of).

The ingredients of ox-gallstones revealed by the foregoing analyses were the following :—

Glycocholate of soda.
Cholonate of soda.
Salt of resinous acid related to the foregoing.
Cholic acid, partly combined with lime.
Choloïdic acid.
Cholochrome, free and combined.
Traces of cholesterin and fatty acids.
A new organic compound soluble in ether.

A sulphide, emitting sulphuretted hydrogen with acids.

Lime, as carbonate, phosphate, and in combination with cholochrome and cholic acid.

Magnesia, as carbonate, phosphate, and in combination with cholochrome and cholic acid.

Chloride of sodium.

Chloride of ammonium.

A compound ammoniacal base.

A matter having a very repulsive odour, and another having the flavour of musk.

Iron in the form of oxide and phosphate.

Alumina.

Manganese.

Copper, a trace.

Zinc, in considerable quantity.

The bulk of the calculi was made up of cholochrome; next in amount were the biliary acids and their salts. Then came lime and zinc, and the new organic compound. The rest of the ingredients were present in very small quantities only.

VII.—*On the Effect of Heating Sulphate and Sulphide of Lead in Hydrogen and Carbonic Oxide.*

By George F. Rodwell, F.C.S.

Sulphate of Lead.

In Hydrogen.—In 1824, Arfvedson reduced sulphate of lead by hydrogen, and found that a mixture of lead and sulphide of lead remained, but I am not aware that the exact nature of the reaction is known.

In order to determine this, sulphate of lead was heated to redness by means of a four-jet Bunsen burner, and a current of pure and dry hydrogen passed over it. The hydrogen was passed through potash and nitrate of silver solution, through concentrated sulphuric acid, a chloride of calcium tube, and a tube filled with anhydrous phosphoric acid; a piece of combustion-tubing, about a foot long, containing the sulphate, followed, and to this was ap-

pended a chloride of calcium tube for the water, a potash tube for sulphurous acid and sulphuretted hydrogen, and lastly a chloride of calcium tube to retain any water that might be carried off from the potash-solution.

The error due to the tubing being attacked was found to be much less than might be expected. 1·343 gramme of sulphate of lead was ignited for an hour in a piece of the tubing used; it was then removed, and although the tube was visibly acted on, no difference in weight could be detected. 4·3527 grm. of sulphate ignited for half-an-hour, caused an increase of only ·0015 grm. in the weight of the tube.

At the end of the reduction, the tubes were thoroughly freed from lead by boiling in dilute nitric acid; they were then dried and weighed, and in no instance did the gain exceed a milligramme; so that the error caused by the glass being acted on cannot effect the accuracy of the determinations. Hydrogen was passed through the apparatus until the escaping gas gave no red colour with binoxide of nitrogen; the sulphate was then heated. On first heating, water and sulphurous acid are given off simultaneously, and before the sulphate has attained a red heat, when the sulphide of lead begins to be decomposed. Five minutes' heating completely removes the oxygen and half the sulphur from half a gramme of sulphate, while an hour and half is required to decompose the remaining sulphide, and there is a distinct interval between the end of the evolution of the water and sulphurous acid, and the beginning of that of the sulphuretted hydrogen.

That a mixture of lead and sulphide of lead, and not subsulphide of lead, remains after the first part of the decomposition, was proved by repeatedly stopping the reduction when the oxygen and half the sulphur had been removed, and before any trace of sulphuretted hydrogen was evolved; on examining the residue, numerous globules of metallic lead were always apparent.

The sulphate only must be heated, and the water driven into the chloride of calcium tube by the current of gas; for if the tube in advance of the sulphate is heated, decomposition of sulphurous acid ensues; it is necessary, therefore, to heat the sulphate till the water and sulphurous acid have been eliminated, then to turn out the gas, and continue the current of hydrogen till all the water has been carried into the chloride of calcium tube, when the residual sulphide may be heated. On account of this necessity of allowing the water to be carried slowly into the chloride of calcium tube,

the anterior end of the combustion tube was drawn out so as to be connected to the chloride of calcium tube by caoutchouc, and the use of a cork, which would have absorbed water, thus obviated. Towards the end of the reduction, cubes and octohedra of sulphide of lead were found sublimed in the tube.

The mean of a number of determinations gave the following:—

Lead	66·8186
Water	17·3630
Sulphurous acid	10·3416
Sulphuretted hydrogen	5·4712
	99·9944

This agrees with the equation—

$$2(PbO,SO_3) + H_7 = Pb_2 + SO_2 + HS + 6HO,$$

which requires—

Lead	66·8171
Water	17·3969
Sulphurous acid	10·3092
Sulphuretted hydrogen	5·4768
	100·0000

2. *In Carbonic Oxide.*—The same arrangement of apparatus was used for the reduction by carbonic oxide, except that the chloride of calcium tube for collecting water was not required. The carbonic oxide was prepared by Fownes' method, and before drying was passed through potash-solution to remove sulphurous acid; the drying was effected by concentrated sulphuric acid, chloride of calcium, and anhydrous phosphoric acid—and the products were collected in a potash tube.

If it were possible to heat every particle of a mass of sulphate of lead to the same temperature at the same time in carbonic oxide, it would be decomposed according to the equation—

$$2(PbO,SO_3) + 6CO = Pb + PbS + SO_2 + 6CO_2.$$

In this reduction, as also in that by hydrogen, three-fourths of the oxygen are removed by the reducing agent, and the remaining fourth goes off with half the sulphur as sulphurous acid; but there is a difference in the two reductions in one respect: for inasmuch

as the affinity of hydrogen for oxygen is greater than that of carbonic oxide for oxygen, it happens in the former case that the oxygen is rapidly removed, and at a comparatively low temperature; while in the latter, five or six times as long a time, and a much higher temperature, are requisite to effect the same result; the consequence of this is that, in the reduction by hydrogen, the temperature does not rise high enough for the first formed portions of sulphide of lead to decompose the sulphate above it, while in that by carbonic oxide, the heat is sufficiently intense, and the reduction sufficiently slow, to allow the sulphide first produced, where the tube is hottest, to act upon the sulphate resting upon it.

Twenty-five determinations were made, but the results were by no means concordant or satisfactory. The best four and their mean are given:—

Residue.	*Products.*
73·3489	50·2045
73·5323	49·4433
73·3160	49·3708
73·5095	50·0306
Mean = 73·4266.	Mean = 49·7623.

Sum = 123·1889.

The determination of the sulphurous acid invariably gave rather less than the theoretical amount; but knowing, as we do, that the products consist of carbonic and sulphurous acids, 100 parts of sulphate of lead and 23·1889 of carbonic oxide, must produce—

Lead . . .	68·3586	
Sulphur . . .	3·8858	Residue = 73·4266
Oxygen . . .	1·1822	
Sulphurous acid . .	13·3226	
Carbonic acid . .	36·4397	Products = 49·7623
	123·1889	

This agrees with the equation, $19\,(PbO,SO_3) + 48CO = Pb_8 + 4PbO + 7PbS + 12SO_2 + 48CO_2$, in which 16 equivalents of PbO,SO_3 are decomposed by 48 of CO, according to the equation $2(PbO,SO_3) + 6CO = Pb + PbS + SO_2 + 6CO_2$, and an equivalent of the sulphide produced acts upon 3 eq. of sulphate, according to the well-known equation, $3(PbO,SO_3) + PbS = 4PbO + 4SO_2$.

The full equation given above requires—

Lead	68·3586	
Sulphur . . .	3·8857	Residue = 73·3545
Oxygen . . .	1·1102	
Sulphurous acid . .	13·3226	
Carbonic acid . .	36·6374	Products = 49·9600
	123·3145	

The oxide of lead seems to form lead-glass as soon as produced, and thus escapes decomposition by the carbonic oxide.

The best results were always obtained when the sulphate was placed in the tube in as much of a mass as possible; when spread out thinly, more oxide of lead appeared to be formed, and the results were exceedingly irregular; but when we remember that sulphide decomposes sulphate of lead according to three distinct equations; that oxide of lead decomposes the sulphide; and lastly, that the manner of placing the sulphate in the tube, the thickness of the glass, and the method of heating, all influence the reduction of the sulphate; it is quite obvious that we can give no definite equation by which in practice sulphate of lead is decomposed by carbonic oxide.

Sulphide of Lead.

The greatest difficulty was experienced in the preparation of sulphide of lead. I do not believe it possible to procure it in a state of purity by precipitating a lead-salt by sulphuretted hydrogen, and drying the precipitate in the air. I invariably found that oxygen had been absorbed.

Two specimens of sulphide of lead prepared by precipitating a solution of the acetate by sulphuretted hydrogen, and drying over a water-bath, were found to gain the following amounts in the air, the time of heating at each different temperature varying from five to nineteen hours.

Oxygen absorbed per hour by 100 parts of sulphide of lead:—

	I.		II.
At 50°C.	·0060	.....	·0086
„ 55°C.	·0089	.....	·0120
„ 60°C.	·0134	.....	·0180
„ 70°C.	·0316	.....	·0405
„ 80°C.	·1017	.....	·1035
„ 100°C.	·1058	.....	·1082
„ 110°C.	·1260	....at 125°C.	·0295
„ 120°C.	·1319		
„ 130°C.	·1400		
„ 150°C.	·1213		
When near 150°, sulphurous acid began to be evolved.		When near 125°, sulphurous acid began to be evolved.	

The amount of surface had nothing to do with the quantity of oxygen absorbed; for sulphide of lead exposing a surface of four square inches gained no more than when the surface was only one square inch.

As soon as sulphurous acid began to be given off, the heating was discontinued; on gently heating some of each of the above sulphides with very dilute hydrochloric, acetic, or tartaric acid, sulphurous acid was evolved, and lead found in solution, proving that the oxygen absorbed had formed *sulphite of lead*, and not sulphate, as is generally stated.

On one occasion, sulphide of lead, which was exposed to a temperature of 135° C., was found to be glowing, and when blown upon, became red-hot, like ignited charcoal, while large quantities of sulphurous acid were evolved; when removed from the air-bath, the ignition quickly ceased, nor could it be again produced by heating the sulphide to the same temperature.

When sulphuretted hydrogen is passed into a solution of acetate of lead, the precipitated sulphide carries down a quantity of acetate with it, so that the supernatant fluid is often entirely free from lead, but on washing the precipitate, a good deal of acetate is found in the washings.

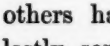
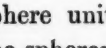
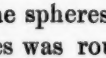
Pure sulphide of lead was prepared in the following manner:—

A rather dilute solution of the acetate or nitrate was precipitated by sulphuretted hydrogen; and the sulphide was thoroughly washed, suspended in cold water through which sulphuretted hydrogen was passed to saturation, then allowed to settle, again washed, and dried at a temperature below 100° C.; when dry, it was heated in a current of dry sulphuretted hydrogen; and finally,

in pure and dry hydrogen, to remove any traces of sulphuretted hydrogen, and of sulphur, that might have been carried down during the precipitation.

1. *In Hydrogen.*—When sulphide of lead, which has been dried at 100° C., is heated nearly to redness in hydrogen, carbonic oxide, or carbonic acid, it contracts to about two-thirds its original bulk, changes from black to a light grey colour, and aggregates into a mass, small pieces of which, a centimetre thick, were found to bear a weight of half a kilogramme, and sometimes as much as a kilogramme, without being crushed to powder.

If the heating is continued, the whole mass becomes crystalline throughout. With pure sulphide of lead, this was found to take place when (1), 1·2391 (2), 1·4219 per cent. of sulphur had been lost; but the loss of sulphur has nothing to do with it, for sulphide of lead heated in carbonic acid likewise becomes crystalline.

The crystals were very lustrous and sparkled in the light; they were seen under the microscope to consist of cubes, octohedra, and tabular crystals with flat and rounded ends—the latter were very noticeable. First there were tables with a rounded end simply  ; a kind of hemisphere was attached to some  ; others had a sphere united by one point only  ; and lastly, some of the spheres were seen by themselves . Only one end of the tables was rounded or had the sphere attached, the other was always flat. A number of crystals, similar to those in the mass, were found sublimed in the tube; but the crystals were largest when the reduction was continued till very little sulphide remained, when a few sparkling black crystals were seen floating on the surface of the melted lead.

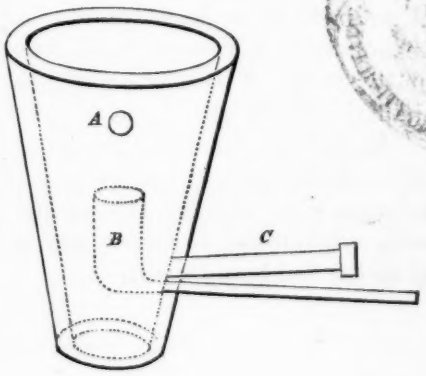
2. *In Carbonic Oxide.*—Sulphide of lead, from which any possible trace of oxygen was removed by previous heating to low redness in hydrogen, was heated in carbonic oxide. Great care was taken to remove the whole of the oxygen from the apparatus before heating; for this purpose, the gas was passed through the apparatus for from half to three-quarters of an hour, a tube containing pyrogallate of potash was then introduced, and the current of gas continued for some minutes. The pure sulphide lost by being heated to redness for an hour in carbonic oxide (1), ·5964 (2), ·4042 per cent. of sulphur; the sulphide was aggregated into a mass, and was crystalline throughout, the crystals being of the same form as those produced by heating the sulphide in hydrogen.

It is stated by Gmelin, that carbonic oxide is decomposed by a red heat; therefore, before submitting sulphide of lead to the action of the gas at a higher temperature than that produced by a four-jet Bunsen burner, it was thought as well to try whether the gas would stand a red heat without suffering decomposition; if it would not, the experiment would of course be fallacious, because we should be acting on the sulphide with a mixture of finely divided carbon and oxygen gas.

In order to determine this, carbonic oxide was passed through a piece of combustion-tubing, which was heated along a foot of its length to bright redness by charcoal. After half an hour's heating, the tube was considerably bent, but no trace of carbon was apparent.

Sulphide of lead was heated to redness by charcoal in carbonic oxide for half an hour; it was found to have lost ·1623 per cent. of sulphur; the mass was very hard; small pieces of it, a centimetre thick, bore a weight of a kilogramme and a half without being crushed; there was no appearance even of the commencement of fusion. It is generally stated, that sulphide of lead fuses at a red heat, but I did not find that fusion ensued before it was heated to whiteness. Sulphide of lead was next submitted to the action of carbonic oxide, at a more intense heat than that produced by ignited charcoal, in a small clay furnace, which, as it allows a piece of porcelain tubing to be heated to whiteness on an ordinary working table, and costs less than a shilling, I may, perhaps, be pardoned for describing somewhat at length.

The furnace was made from a clay crucible 6 inches high, and $3\frac{1}{2}$ internal diameter at the top; two holes, A, were bored at $1\frac{1}{2}$ inches from the top, opposite each other; the internal diameter here was $3\frac{1}{4}$ inches, so that $3\frac{1}{4}$ inches of porcelain tubing can be heated; at $1\frac{1}{2}$ inches from the bottom, a hole of this shape was bored, into the lower part of which the stem of the pipe B fitted; into the upper part, the nozzle, C, of a pair of bellows; B is one of the



large Dutch pipes, the bowl of which is 2 inches long by 1 inch in diameter; it is easily introduced through the body of the furnace, and placed in the position shown in the figure, which is one-fourth the real size. By means of this pipe, oxygen gas is introduced into the furnace. The furnace is filled with red-hot pieces of charcoal about the size of hazel-nuts, which are brought to intense ignition by the bellows. When the porcelain tubing and the pipe-bowl are at a red heat, a current of oxygen from a gas-holder is turned on; the pipe-bowl, which is 1 inch below the porcelain tube to be heated, is stuffed full of pieces of the pipe stem, of the same length as itself, in order to cause the oxygen to issue from as large a surface as possible, and also to compel it to come in contact with a very large red-hot surface in passing through the pipe-bowl; the consequence of this is, that the oxygen when it issues from the pipe, is at a very high temperature, and the porcelain tube is soon brought to a most intense state of white hot ignition. The surface of the pipe-bowl (= ·7854 square inch) from which the oxygen issued, was found to be fused after once using it, the whole time of passing the oxygen not amounting to a quarter of an hour; the outside of the porcelain tube heated was glazed. This small furnace is easily constructed; a bright white heat may be kept up so long as there is a supply of oxygen, and so long as the materials remain unfused.

Sulphide of lead was placed in a porcelain tube, and heated in carbonic oxide by means of the above furnace; the time of heating was half an hour, at intervals during which the tube was raised to whiteness; at the end of the experiment, the sulphide had lost ·3892 per cent. of sulphur; it was fused, and very brilliant sparkling cubes (some of which had sides of $\frac{1}{10}$th of an inch) were found in the fore part of the tube: had the heating been continued much longer, these would have stopped up the tube. A second experiment in which the sulphide was similarly treated gave a loss of ·4830 per cent. of sulphur.

In each of the above experiments in which sulphide of lead was heated in carbonic oxide, the products were passed into potash-solution, which became yellow, and on treating it with a dilute acid, sulphuretted hydrogen was evolved, proving that *bisulphide of carbon* had been formed.

VIII.—*On the Atomic Weights of Cobalt and Nickel.*

By William J. Russell, Ph. D.

1.—*Cobalt.*

When oxide of cobalt is ignited in the air, no constant compound is obtained, the weight of oxide varying more or less after each ignition. Sometimes the weight approaches very nearly that required by the supposition that the oxide has the composition $Co_3 O_4$; at other times it diminishes so as only slightly to exceed the weight it would have if the whole of it were pure protoxide. This alteration in weight may be made to take place at pleasure by varying the intensity of the heat, and the rate at which the oxide is cooled. When the oxide is strongly ignited over a blast-lamp, and rapidly cooled, its composition agrees very nearly with that of the protoxide, but when slowly cooled or less strongly heated, it is found to contain a larger amount of oxygen. It appears probable from these facts, that the higher oxides of cobalt are decomposed at a high temperature, and reproduced to a greater or less extent as the oxide cools.

Again, if oxide of cobalt is strongly heated in a crucible filled with carbonic acid, and allowed to cool without coming in contact with the air, it undergoes a complete change of colour, passing from black to a rather light brown. This change of colour was first mentioned to me by my friend Dr. Dexter. I have carefully examined this brown substance, and have proved by numerous analyses that it is pure protoxide of cobalt. To show the constancy of this compound, and the ease with which it may be formed, I cite the following experiments:—1·3971 grms. of black oxide of cobalt were heated for five minutes in a platinum crucible over a blast-lamp in a current of carbonic acid, then allowed to cool in an atmosphere of this gas, and weighed. Its weight was 1·3017. This same portion of oxide was then heated in the air, so to reconvert it into black oxide, and then again heated in carbonic acid: it now weighed 1·3015.

No. of Experiment.	Quantity taken.	Weight after ignition in CO_2.	CoO per cent.
1.	1·3971	1·3017	93·17
1.	do. (reheated)	1·3015	
2.	1·1114	1·0357	93·18
3.	1·0103	0·9414	93·19

The last column shows the percentage amount of protoxide contained in this specimen of black oxide, as deduced from these experiments.

In order to ascertain whether the oxide would undergo any further change by being heated for a longer time in carbonic acid, a weighed portion of the brown oxide was heated over the blast-lamp for three-quarters of an hour, and the heat rendered as intense as possible by surrounding the platinum crucible with a black lead one; but this produced not the slightest alteration in the weight of the oxide. Again, that this brown oxide is unmixed with any of the higher oxides of cobalt, is proved by dissolving it in hydrochloric acid and distilling the acid into water containing iodide of potassium and starch, when no trace of blue colour is produced.

The composition of this compound was ascertained by reducing known weights of it by means of hydrogen. The first two experiments for instance gave the following results:—

1·2612 grms. of brown oxide gave 0·9915 of metal.
0·8193 grms. do. do. 0·6441 do.

From these we deduce the following percentage:—

Composition, 1st expr. Cobalt, 78·61.
2nd „ do. 78·61.

These experiments were made soon after Schneider* published his paper on the Atomic Weight of Nickel and Cobalt; and as they differ so widely from the number 78·94, which should have been obtained, had his equivalent of 30 been correct, I was induced to undertake a series of experiments to establish, if possible, the true atomic weight of this metal. The difficulty which had previously existed in preparing a pure oxide of cobalt, prevented the atomic weight being obtained by so simple a method as that of the reduction of the oxide by hydrogen. The method adopted by Rothoff, who, I believe, was the first to make any experiments on the atomic weight of cobalt, was to estimate the amount of chlorine in a known weight of chloride of cobalt by precipitation with nitrate of silver. The atomic weight he deduced from his experiments was 29·45. Schneider, by estimating the amount of cobalt and carbon in the oxalate, deduced the number 30 as the true atomic weight. Dumas†, who has still more recently investigated this subject, adopted a process

* Pogg. Ann., 101, 387. † Ann. Ch. Pharm., 113, 20.

similar to that used by Rothoff, only using a standard solution of nitrate of silver instead of weighing the chloride of silver formed. He deduces from his experiments, which vary from 29·50 to 29·57, the number 29·5 as the probable atomic weight of cobalt.

The properties of this brown protoxide of cobalt well adapt it for being used as a means of determining the atomic weight. It is easily obtained, is of very definite composition, but slightly hygroscopic, and easily reduced to the metallic state. At ordinary temperatures, it appears to undergo but very slight alteration in composition; some specimens of it have been kept for many weeks without absorbing any trace of oxygen; another specimen prepared some eight or nine months ago, has now been found to contain a trace of some higher oxide.

It naturally suggested itself as an interesting question whether the carbonic acid acts otherwise than merely mechanically, simply preventing the contact of oxide, after it has been heated, with the air, or whether the presence of a foreign atmosphere is the principal cause of the ready giving off of the excess of oxygen. The experiments I have made on this subject show that the carbonic acid is not necessary to the formation of the protoxide, but that it is a question of temperature, all the higher oxides of this metal being decomposed when strongly heated. I proved this in the following manner:—A small platinum crucible was nearly filled by pressing into it oxide of cobalt, and strongly heated over a blast-lamp for ten minutes; it was then very rapidly cooled by immersing the crucible in cold water. When quite cold, the oxide was turned out of the crucible, and it was found that, although the surface was black, the interior portion had the characteristic brown colour. By this process also, I have obtained an oxide which analysis has shown not to vary above $\frac{1}{10}$ or $\frac{2}{10}$ per cent. from the oxide prepared by the help of the carbonic acid.

In the following experiments on the atomic weight of cobalt, three different specimens of the black oxide were used. They were sold as being nearly pure, but contained a considerable amount of impurity, the nature and quantity of which varied in each specimen. The following is the process which was adopted to purify them:—The oxide was first dissolved in hydrochloric acid, then evaporated to dryness, and heated for several hours. The chloride was then dissolved up in water containing a few drops of hydrochloric acid, and the insoluble silica filtered off. This process was repeated to ensure the removal of the silica. A

considerable amount of sulphurous acid was now passed into the solution of the chloride, and the liquid allowed to stand for some days in a warm place. The sulphurous acid was then removed by boiling, and after adding hydrochloric acid, the liquid was thoroughly saturated with hydrosulphuric acid, and again allowed to stand for several days in a warm place. If more than a very small amount of precipitate was obtained with the first specimen of cobalt, the iron was then precipitated by ammonia; and the remaining metals were converted into sulphides, and digested for some length of time with dilute hydrochloric acid to remove the manganese. The cobalt was next converted into Claudet's salt, and then boiled with strong hydrochloric acid for some days, the acid being changed from time to time. In order to purify still further this salt, it was dissolved in water slightly acidulated with hydrochloric acid and recrystallized. The salt was now heated first in air and afterwards in hydrogen; the metal was then dissolved in nitric acid, and the solution was evaporated to dryness, and strongly heated. The carbonic acid used was prepared from white marble, and purified and dried by passing, first through two wash-bottles containing pumice-stone and a solution of carbonate of potash, then through another wash-bottle containing sulphuric acid, and lastly through a U-tube containing pumice-stone moistened with sulphuric acid.

The hydrogen was prepared by using thin sheet-zinc, which appeared to be free from arsenic, and was passed, first through a wash-bottle containing a dilute solution of caustic potash, then through one containing a solution of nitrate of silver, and afterwards dried by passing through a third bottle partly filled with sulphuric acid, and lastly through a U-tube containing pumice moistened with sulphuric acid. To break up the stream of gas, small pieces of pumice-stone were placed in all the bottles.

Both these gases passed along the same tube into the crucible containing the cobalt, this tube being connected by means of a T-piece with both apparatus. There was also another means of escape for the gases, namely, by a tube passing through the cork of the last washing bottle, and bent down so as to dip some distance into sulphuric acid. Thus, when the sides of either of the caoutchouc tubes connecting the T-piece with the last drying of either apparatus were pressed together by a clamp, the gas then escaped, bubbling up through the sulphuric acid. By this contrivance, either gas could be passed into the crucible

without admitting the air. The reason for adopting this method was the difficulty and loss of time experienced in cooling the platinum crucible full of hydrogen, the platinum causing the gas to burn, and in some cases the moisture thus formed was found even to affect the weight of the cobalt. To obviate this, the oxide of cobalt, after being reduced by hydrogen, was allowed to cool in an atmosphere of carbonic acid.

The oxide of cobalt was weighed in a small cup made of platinum foil; the foil was first heated in nitric acid to remove any foreign metal adhering to its surface, and before being used, it was proved that the weight of the cup remained unaltered after being heated both in air and in hydrogen. In order to heat this cup without bringing it in contact with the gas flame, it was placed inside a platinum crucible in the bottom of which there was a piece of pipeclay; this prevented the direct contact of the two platinum surfaces, which, after being strongly heated, are apt to adhere together with considerable force. A cover of platinum foil was carefully fitted on to the crucible, and a hole in the centre admitted the tube conveying the gas. To prevent, however, the stream of gas playing directly on the oxide, a small piece of platinum-foil was fastened in front of the orifice, so that the gas striking against it was more uniformly spread over the interior of the cup, and any mechanical carrying away of the oxide was prevented.

The general process adopted in the experiments was as follows: The weight of the platinum cup was first carefully ascertained, then, after introducing the necessary quantity of black oxide, the cup was placed inside the crucible, and the air thoroughly expelled by carbonic acid. The crucible was now heated as strongly as possible over a blast-lamp for about a quarter of an hour, then allowed to cool, a brisk current of carbonic acid being kept up the whole time. The cup was afterwards removed to the balance case, the bottom of which was covered with a layer of chloride of calcium, and carefully weighed. By repeating this operation two or three times, a constant weight of the protoxide was obtained. The reduction by hydrogen was effected, first at a comparatively low temperature, the crucible being heated only by a single Bunsen's burner for half to three-quarters of an hour, and then by a blast-lamp for about a quarter of an hour; in this way the metal was obtained in a dense form and hardly at all hygroscopic.

The first specimen of cobalt gave the following results when treated as above described :—

No. of Experiment	Weight of Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	2·1211	1·6670	78·591
2.	2·0241	1·5907	78·588
3.	2·1226	1.6673	78·550
4.	1·9947	1·5678	78·598
5.	3·0628	2·4078	78·614
		Mean	78·588

After making these determinations, the remaining portion of the oxide was again dissolved in hydrochloric acid, and subjected a second time to a process of purification similar to the one it had already undergone. The following are the results obtained from the oxide thus treated :—

Cobalt.

Specimen No. 1—2nd Purification.

No. of Experiment	Weight of Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	2·1167	1·6638	78·603
2.	1·7717	1·3924	78·591
3.	1·7852	1·4030	78·591
		Mean	78·595

Again, the remaining portion of this oxide was subjected to a third purification, and the amount of metal in the oxide determined.

Cobalt.

Specimen No. 1—3rd Purification.

No. of Experiment	Weight of Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	1·6878	1·3264	78·588
2.	2·2076	1·7350	78·592
		Mean	78·590

The second specimen of cobalt, after being treated in the same manner as the first, gave the following results:—

Cobalt.

Specimen No. 2.

No. of Experiment	Weight of Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	2·6851	2·1104	78·597
2.	2·1461	1·6868	78 598
			Mean 78·597

The third specimen gave the following results:—

Cobalt.

Specimen No. 3.

No. of Experiment	Weight of Protoxide taken	Weight of Metal found	Amount of Metal in 100 parts of Protoxide
1.	3·4038	2·6752	78·595
2.	2·2778	1·7901	78·589
3.	2·1837	1·7163	78·596
			Mean 78·593

The following numbers are the means of each of the foregoing series of determinations:—

78·588
78·595
78·590
78·597
78·593

Mean..... 78·5926

If now we take this last mean as representing the true amount of metal in the oxide, and calculate from it the atomic weight of cobalt, we find it is represented by the number 29·370.

II.—Nickel.

For determining the atomic weight of this metal, three different specimens of nickel were employed. The following is the method adopted for obtaining the metal in a pure state. The first part of the process is similar to that already described for the purification of the cobalt, namely, dissolving in hydrochloric acid, and separating the silica, arsenious acid, and other metals precipitable from an acid solution by hydrosulphuric acid. Having removed any of these impurities that might be present, the solution was diluted very considerably and saturated with chlorine, carbonate of baryta added, and the excess of this salt removed by dilute sulphuric acid. The nickel was then precipitated by means of pure oxalic acid prepared by decomposing oxalate of ethyl with water. The oxalate of nickel thus obtained was dissolved in ammonia, and then allowed slowly to deposit from this solution. It was then washed and dried, and, after being strongly heated, was dissolved in nitric acid, the solution evaporated to dryness, and the nitrate decomposed by heat. As the oxide of nickel obtained in this way is generally regarded as the pure protoxide, and as I found that on heating it over a Bunsen's burner in a platinum capsule, in the same way as that adopted in heating the cobalt, the weight of the oxide and capsule remained constant, I supposed the oxide to be pure protoxide. For instance, three consecutive experiments gave the following numbers as the amount of metal in the oxide: 78·461, 78·472, and 78·465. The oxide in this case was prepared by heating the nitrate to a red heat for several hours, and well stirring it, and although these three specimens were heated for different lengths of time, still this produced no appreciable difference of composition, as is shown by these numbers; it was found, however, that if different temperatures were employed, considerable variations in the amount of metal contained in the oxide occurred. If, for instance, the oxide were prepared by employing a dull red heat, four consecutive experiments showed that it contained only the following amounts of metal, 78·418, 78·421, 78·442 and 78·418, and however long the heat was continued it did not change the composition; in fact, the second of these four specimens was heated for twelve hours longer than the first. Further, on boiling the oxide prepared in

this way with hydrochloric acid, and passing the products of the distillation into a solution of iodide of potassium, free iodine was always liberated. I next tried whether I could obtain a pure protoxide by employing a much higher temperature, and was quite successful in so doing. When oxide of nickel is very strongly heated over a blast-lamp, all the higher oxides are decomposed and pure protoxide remains behind. On dissolving the oxide thus obtained in hydrochloric acid no chlorine is liberated. This complete decomposition of the higher oxides is however not very easily effected; the heating must be continued for a considerable length of time, the oxide occasionally stirred, and the heat of the blast-lamp rendered as intense as possible. In several instances I traced by analysis this gradual loss of oxygen by continued heating, the amount of metal in the oxide increasing till, as will be seen in the following experiments, it reached 78·59, and then, however long the heating was continued, no further alteration took place. This continued heating produces a very marked change in the oxide: it diminishes greatly in bulk, and assumes, I believe, always when pure a bright green colour.

This pure protoxide of nickel was at first prepared by heating the ordinary oxide in carbonic acid in the same way as that adopted in preparing the oxide of cobalt; but it was found that the carbonic acid was in no way necessary, the oxide of nickel differing from that of cobalt in having no tendency to reabsorb, on cooling, the oxygen which it has lost at a high temperature. This difference of property of the two oxides is well shown by the following experiment made with the pure oxide of nickel:—

Weight of the oxide after heating over blast-lamp				1·8296
Do.	do.	exposed to low red heat for	1½ hours	1·8296
Do.	do.	do.	½ hour	1·8296

Neither did this continual heating at a low temperature produce the least change in the green colour of the oxide.

In making the following analyses, it was however found convenient to pass a stream either of carbonic acid or of air into the crucible containing the oxide, while it was being heated, in order to prevent any reducing gases from the flame acting on the oxide; many analyses showed that the composition of the oxide was the same whichever of the gases was used.

The following determinations were made with the same precau-

tions and in the same way as that adopted with the oxide of cobalt. The oxide of nickel was heated so as to convert it into a very nearly, if not quite, pure oxide, before taking a weighed quantity for experiment.

Nickel.

1st Specimen.

No. of Experiment.	Weight of Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·0820	1·6364	78·597
2.*	—	—	—
3.	2·0956	1·6468	78·584
4.	2·0148	1·5838	78·608
		Mean	78·596

The second specimen of nickel was purified three times by the process already described. Unfortunately, I have no determinations made after the first and second purifications; but the oxide, after having undergone the three purifications, gave the following results :—

Nickel.

2nd Specimen—3rd Purification.

No. of Experiment.	Weight of Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·2069	1·7342	78·581
2.	2·2843	1·7952	78·589
3.	2·1329	1·6761	78·583
		Mean	78·584

A comparison of these two tables will show how very slight is the effect produced by increasing the number of purifications, the difference of the means of the two series being only ·012.

* The second experiment I have omitted in the table, owing to its not having been made at so high a temperature as the others, so that a trace of a higher oxide appears to have escaped decomposition. When making this experiment, I was not aware of the high temperature necessary. The results of the experiment are as follows :—

No. of Experiment.	Weight of Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
2.	2·6921	2·1151	78·567

The third specimen of nickel, after one purification, gave the following results:—

Nickel.

3rd Specimen—1st Purification.

No. of Experiment.	Weight of Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·2783	1·7911	78·616
2.	2·1434	1·6845	78·590
3.	2·4215	1·9030	78·588
		Mean	78·598

The mean of this series of experiments is almost identical with that of the first series. I therefore resolved to repurify the remainder of this oxide, in order to see if a decrease in the number would again take place. The following are the results obtained:—

Nickel.

3rd Specimen—2nd Purification.

No. of Experiment.	Weight of Oxide taken.	Weight of Metal found.	Amount of Metal in 100 parts of Oxide.
1.	2·1859	1·7179	78·590
2.	2·0088	1·5788	78·594
3.	2·0839	1·6379	78·597
4.	2·6560	2·0873	78·588
		Mean	78·592

This second purification can hardly be said to have altered the mean result of these experiments. We have then the following numbers as the means of the different series of experiments:—

1st Specimen	78·596
2nd Specimen—3rd Purification . .	78·584
3rd Specimen—1st Purification . .	78·598
Ditto 2nd Purification . .	78·592

If now we allow the mean of each series of experiments to have an equal value, the general mean will be 78·592; and, taking this number as representing the true amount of metal in the oxide, it gives, as the atomic weight of nickel, the number 29·369.

From the foregoing experiments, it appears then that the atomic

weights of nickel and cobalt are identical and somewhat lower than the number hitherto in use.

As the alteration in the weights obtained would have been so slight, it was not thought worth while to reduce the weighings to what they would have been in a vacuum.

In conclusion, my best thanks are due to my assistant, Mr. Gill, for the very valuable aid he has given me in carrying out this research.

IX.—*On the Determination of the Amount of Organic Matters in Drinking Waters, by means of a Standard Solution of Permanganate of Potash.*

By Dr. Woods, Army Medical Staff.

The deleterious effects resulting to the health of communities from the presence of organic matter in drinking waters, renders the detection of this contamination a subject of serious importance.

The mere presence may be detected, either by a solution of chloride of gold, or by one of permanganate of potash, a fact already pointed out by several observers, and now widely known.

The determination of the precise amount of organic matter, by the gravimetrical method, offers considerable difficulty, owing to the volatilization of some of the constituents of the salts with which it is ordinarily mixed. The following method, based on the oxidizing power of a solution of chamæleon, and tested by a considerable number of experiments, shows the value of a certain weight of permanganate of potash, as compared with a certain weight of organic matter. Elevation of temperature aids in a high degree the oxidizing power of the salt. Some compounds, owing to their fixed character, or the already high degree of oxidation to which they have attained, remain unaffected; and in all cases a very considerable lapse of time is found to be necessary to complete the process.

All waters I have hitherto examined, decolorized, owing to the organic matters which they contained, certain proportions of the test-solution; and as such organic matters are in most cases similar in character, being derived either from the soil or from sewage contamination, the deoxidizing power which they exert,

is most likely in all cases to produce an influence proportionate to their quantity.

To arrive at the value of a known weight of permanganate of potash, with reference to organic matter, I first determined, by weight, the amount of the latter in a certain measure of sewage. Of a similar sewage fixed quantities were taken, and after dilution with varying amounts of water, rendered acid by sulphuric acid; the action of a standard solution of permanganate of potash was noted.

The points which I found most necessary carefully to attend to, as influencing the results derived from my experiments were:—

1st. The degree of acidity of this solution.

2nd. The temperature of the fluid during the addition of the oxidizing solution.

3rd. The period occupied by the experiment.

With reference to the degree of acidity of a fluid, as affecting the amount of the test-solution required to produce a colour lasting for a certain period, I found that whilst 300 cc. of water, acidified by 2 cc. of sulphuric acid, sp. gr. 1·614*, and heated to 140° Fah., required but 0·32 cc. of the standard solution which I used; 300 cc. of the same water, with 10 cc. of acid, required 6·6 cc. to produce in each case a colour lasting for half an hour.

The fact that the degree of acidity of a fluid affects in a corresponding degree a solution of chamæleon is, of course, well known, and I merely allude to the subject here, as demanding special attention, owing to the very small amount of organic matter (= 0·24 cc. of the test-solution) present in a litre of some waters which I have examined.

Variations in the temperature of the liquids exercised a marked influence on the permanency of the colour produced, enduring for a longer or shorter period; thus a shade of colour, which at a temperature of 140° would have remained permanent for half-an-hour, was rapidly destroyed by raising the temperature to 160°; a change of temperature equal to 10° or 20° Fah., producing marked effects. Now, as the contact of the oxidizing solution with the organic element must be more or less prolonged, to avoid error, it was found necessary that a fixed temperature should be taken for all experiments.

* The sp. gr. of the acid used in all the experiments = 1·614. The quantities of the test-solution necessary to produce permanent coloration were found to vary in each case, with varying quantities of acid, and not to follow any fixed relation that could be observed.

A large number of experiments, in which the liquid containing organic matter and a proportion of sulphuric acid, was heated to 140° Fah., the heating apparatus being removed prior to the addition of the test-solution, gave as results:—that 1·24 cc. of the test-solution, containing 0·00124 grms. of permanganate of potash, produces a colour permanent for half-an-hour, in a liquid made up of 300 cc. of water, 2 cc. sulphuric acid, and 0·005 grms. organic matter.

Deducting 0·24 cc., the amount, as determined by previous experiment, decolorized by a corresponding quantity of acid and pure distilled water, we have 1 cc. or 0·001 grms. of permanganate of potash, equivalent to 0·005 grms. organic matter. To ascertain the correctness or otherwise of the results just stated, I instituted two other series of experiments. In the first, I added to known quantities of water sewage and acid, at ordinary temperatures, successive small quantities of the standard test-solution, until a colour permanent for 12 hours was produced. In the second series, I added at one time the total quantity found necessary in the first. The results may be briefly stated as follows:—

1st. That the time necessary for the total oxidation of organic matter in waters at ordinary temperatures, varies with the amount, the decolorization of the oxidizing solution requiring from 24 to 48 hours.

2nd. That within a minute proportion, varying from 0·01 to 0·02 cc., twice the amount of the test-solution was required to complete the experiment at ordinary temperatures, to that found necessary when the liquid was heated. A proportion of the permanganate solution however undergoes deoxidation by causes independent of the action of organic matter, the amount depending on the value of each addition, or in other words, on the strength of the solution. Thus I found, that in an acid liquid, made up of 300 cc. of water and 2 cc. of sulphuric acid, a proportion of the test-solution equal to 0·1 cc., was destroyed in each successive period of 24 hours, when the addition did not exceed 0·50 cc.; but that when larger quantities were added, the amount decomposed might equal 0·50 cc. This variable decomposition, therefore, renders results derived from experiments performed on waters at ordinary temperatures, of less value than those deduced when the liquid is heated, and the time occupied by the experiment reduced to a minimum.

In the drinking waters which I have examined, employing an elevated temperature, I found that the smallest quantity required

of the test-solution was 0·24 cc., and the largest 7·5 cc., to produce a colour permanent for half-an-hour, in a litre of the fluid submitted to examination; thus indicating the presence in one case of 0·0840, and in the other of 2·62 grains in a gallon.

The former water, derived from the chalk strata, and furnished by the Chatham Water-works, is thus shown to be, as we should *a priori* expect, an extremely pure liquid, whilst the latter, derived from the same geological series, but taken from a pump in close juxtaposition to a cesspool, is shown to be largely impregnated with organic impurities, and had to be discontinued for household purposes by a family, in whom its use produced serious diarrhœa, which immediately ceased when the purer liquid supplied by the town water-works was substituted. In another water examined, and in which 0·96 cc. of the test-solution were required, affording evidence of the presence of 0·336 grains in a gallon, no bad effects, so far as I could learn, resulted; but in this case filtration was had recourse to previous to use. It is to be hoped future researches will give us a more definite knowledge on this head; but with my present experience, I should reject all waters which afford evidence of the presence of half a grain of organic matter in a gallon, as determined by the test-solution. It must not be left out of view that the presence of iron, in the state of protoxide, in the water, will, if in any quantity, seriously interefere with our deductions, and should therefore be taken into account.

After what has preceded, little need be stated as to the mode of performing the experiment. For ordinary valuation, a solution of chamæleon containing 0·001 grm. in each cubic centimeter will suffice, if made on each occasion immediately prior to being used; but as such a solution undergoes deoxidation by keeping, it should be graduated before employing it in any experiment, in such a manner that 13 cc. will produce a colour permanent for half-an-hour in 300 cc. of pure distilled water, to which 40 cc. of a solution of oxalic acid containing in each cc. 0·00063 grm. and 2 cc. of strong commercial sulphuric acid have been added. A litre of the water whose purity we require to determine, is the most convenient quantity to take. After the addition of 2 cc. of commercial sulphuric acid, the liquid should be heated in a perfectly clean and white porcelain dish to 140° Fah. when any further application of heat must be avoided. The test-solution should then be added, beginning with even minute quantities—one to two drops at a time—and waiting after each addition for the total

disappearance of colour. When a shade persistent for half-an-hour has been produced, we may consider the experiment as at an end. It is convenient and useful to have on the table a second porcelain dish, containing a quantity of the water, by comparison with which we may be made aware of the total disappearance of colour from the liquid under examination. Assuming as correct the conclusions at which I have arrived, namely that 1 cc. of the test-solution corresponds to 0·005 grm. of organic matter, a simple calculation suffices to give us the number of grains in a gallon. Thus, let us suppose 1·24 cc. of the test-solution were required to produce a shade persistent for the necessary time, deducting 0·24 cc. for the quantity corresponding to 1000 cc. of distilled water, and 2 cc. of sulphuric acid, we should have remaining 1 cc. as corresponding to the amount of organic matter present, therefore $1 \times 0{\cdot}005 = 0{\cdot}005$ grm. in a litre, which, multiplied by 70, gives, as a sufficiently accurate result, 0·350 grains in a gallon. When our chamæleon solution is not of the exact titre indicated, we can yet easily determine, from the amount required by the oxalic acid solution of known strength, the volume equivalent to a certain quantity of organic matter. Thus, let us suppose we have used 14 cc. instead of 13 cc. to produce a lasting colour in the oxalic acid solution, then $\frac{13 \times 1}{14} = 0{\cdot}9285$ cc. equal to 0·005 grm. of organic matter.

X.—*On the Action of Sulphuric Acid upon Lead.*

By F. Crace Calvert and Richard Johnson.

It has been generally supposed by scientific men, but we do not know upon what grounds, that metals are less acted upon by acids in proportion to their greater degree of purity, and it naturally follows that smelters strive to attain a continually increasing purity in the metals they produce.

This is especially the case in the manufacture of lead, because

the process which purifies the lead enables the smelter to extract from it other substances, such as silver, rendering the operation profitable in itself. It is, however, very desirable to ascertain whether the opinion generally held respecting the diminished action of acids on metals in proportion to their purity, is really correct as regards lead, and hitherto we are not aware that any experiments have been made with the view of determining this question.

We have therefore thought that it might be interesting in a scientific point of view, as well as practically useful, to study the action of acids, and especially that of sulphuric acid, upon some of the leads of commerce, which, as is well known, are largely employed in the construction of those large chambers in which sulphuric acid is manufactured.

With this object in view, we have instituted a series of experiments to ascertain the action upon lead of sulphuric acid of various degrees of concentration and purity, in different volumes, at various temperatures, and for various periods of time. We have made use of two kinds of commercial lead, choosing as types the two extremes in respect of purity, viz., common sheet lead representing ordinary impure lead, and virgin or Derbyshire pig-lead. We have also thought it desirable to examine the action of sulphuric acid upon chemically pure lead; and we may at once state, as the result of three or four repetitions of each series of experiments, all agreeing closely with each other, that we have arrived at a conclusion directly opposed to the generally received opinion: for we have found that the purer the lead in contact with sulphuric acid, the more is it acted upon. Thus the action on pure lead is from two to three times as great as that upon the common kinds, as will be seen by the following results:—

The analysis of the two classes of lead upon which most of our experiments were made, yielded the following results:—

	Common Lead.	Virgin Lead.
Lead . . .	98·8175	99·2060
Tin . . .	0·3955	0·0120
Iron . . .	0·3604	0·3246
Copper . .	0·4026	0·4374
Zinc . . .	traces	traces
	99·9760	99·9800

Thirty square centimetres of each of the different kinds of lead were acted upon (at ordinary temperature of 18° to 20° centig.), by 50 cubic centimetres of perfectly pure sulphuric acid, and at the end of ten days, the following quantities of lead were dissolved:—

Table No. 1.

Density of the Acid employed.	Common Lead. gr.	Virgin Lead. gr.	Pure Lead. gr.
	I. 0·199	I. 0·400	I. 0·600
1·842	II. 0·207	II. 0·405	II. 0·610
	Mean 0·2030	Mean 0·4025	Mean 0·6050
	I. 0·029	I. 0·048	I. 0·060
1·705	II. 0·021	II. 0·051	II. 0·058
	Mean 0·0250	Mean 0·0495	Mean 0·0590
	I. 0·015	I. 0·028	I. 0·050
1·600	II. 0·016	II. 0·034	II. 0·047
	Mean 0·0155	Mean 0·0310	Mean 0·0485
	I. 0·007	I. 0·015	I. 0·018
1·526	II. 0·006	II. 0·011	II. 0·023
	Mean 0·0065	Mean 0·0130	Mean 0·0205

The next table gives the above results calculated for a metre of surface (instead of 30 centimetres) acted upon by a proportionate quantity of acid (16·666 litres).

Table No. 2.

Density of Acid employed.	Common Lead. gr.	Virgin Lead. gr.	Pure Lead. gr.
1·842	67·70	134·20	201·70
1·705	8·35	16·50	19·70
1·600	5·55	10·34	16·20
1·526	2·17	4·34	6·84

These results leave no doubt that the purer the lead, the more

is it attacked, and that in a ratio which is very curious and instructive.

In another series of experiments made with the same lead, with this difference, that the period was fifteen instead of ten days, the following are the results calculated for a square metre :—

TABLE No. 3.

Density of Acid employed.	Common Lead. gr.	Virgin Lead. gr.	Pure Lead. gr.
1·842	89·00	194·34	279·00
1·705	11 67	16·84	24·00
1·600	6·17	12·17	20·00
1·525	3·17	8·67	8·67

These results confirm the above.

If instead of natural temperature, we operate at a temperature of about 45° centig. for eight days, we still find, as in the preceding instances, that the action of the acid on the purer lead is more energetic than on the ordinary qualities.

TABLE No. 4.

Density of Acid employed.	Common Lead. gr.	Virgin Lead. gr.	Pure Lead. gr.
1·842	418·34	458·50	507·34
1·705	6·84	10·67	13·00
1·600	5·84	6·34	11·84
1·525	3·50	4·84	6·67

The question occurred to us whether the purity of the acid employed had occasioned such unexpected results, and whether the substitution of ordinary commercial acid would not show a different relative intensity of action. We therefore used some acid from the leaden chamber, which had undergone no purification, its density being 1·593. The following results were obtained from two series of experiments continued for fifteen days at a temperature from 45° to 48° centig.

TABLE No. 5.

Density of Acid employed (from leaden chamber).	Common Lead. gr.	Virgin Lead. gr.	Pure Lead. gr.
1·593	I. 11·84	I. 15·84	I. 19·50
	II. 11·34	II. 16·17	II. 19·84

If we employ twice the quantity of acid to the same surface of

lead, other conditions remaining as in the preceding experiment, we find that the action increases in each case with the purity of the lead, but not in the proportion of 1 to 2. The following table (6) gives the mean results of two distinct series of experiments:—

Density of Acid employed (from leaden chamber).	*Common Lead.*	*Virgin Lead.*	*Pure Lead.*
	Quantity of Lead dissolved in 15 days by the action of 33·333 litres of acid upon the square metre of surface.		
	gr.	gr.	gr.
	I. 20·17	I. 22·50	I. 27·00
1·593	II. 22·17	II. 24·34	II. 27·67

We repeated these experiments, employing acid, not as it comes from leaden chambers, but after having been once evaporated in open leaden vessels in which its concentration is commenced commercially. The following table gives the mean of figures obtained from two distinct series of experiments with one volume and with two volumes of this acid. In each experiment, the acid used was obtained from a different source:—

TABLE No. 7.

Density of Acid proceeding from open leaden vessels in which its concentration is commenced in commerce.	*Common Lead.*	*Virgin Lead.*	*Pure Lead.*
	Quantities of Lead dissolved by the action of 16·666 litres of acid for 15 days at temperature of 113° to 122° upon one square metre of metallic surface.		
	gr.	gr.	gr.
	I. 49·67	I. 50·84	I. 55·00
1·746	II. 51·91	II. 54·75	II. 57·41
	Quantities of Lead dissolved by 33·333 litres instead of 16·666 litres of acid, the other conditions remaining as above.		
	gr.	gr.	gr.
	I. 54·67	I. 56·17	I. 59·34
1·746	II. 56·25	II. 58·67	II. 60·67

We have confined ourselves to a few particulars, without entering at length into all the details of our experiments. We may however state that they were well repeated many times, and that we varied the surfaces of lead, the quantities of acid, the temperature, the duration of action, and, in fact, all the conditions of the experiments, and yet we always obtained similar results, from which we draw the following conclusions:—

1st. And this is the principal point to which we invite the

attention of scientific as well as practical men: Of the various kinds of lead existing in commerce, the purer they are, the more are they acted upon by sulphuric acid. Lead chemically pure is more acted upon than any of the others.

2nd. Although it is stated in many works on chemistry, that sulphuric acid only acts sensibly on lead at a temperature of about 195° centig., our experiments tend to prove the contrary, since we find that acid of sp. gr. 1·842 dissolves *cold* 67·134, and even 201 grms. of lead per square metre of surface, and in another instance, that acid of sp. gr. 1·705 takes from the same surface 54, 56, and 59 grms. of lead at a temperature of about 45° centig. only.

3rd. Finally, the action of sulphuric acid upon lead appears, at least when there is no continuous agitation of the mass, not to increase in proportion to the quantity of acid employed. This is probably due to the formation of a layer of sulphate of lead, which to a great extent protects the surface from further action of the acid.

During the progress of the foregoing experiments, the following circumstance came under our notice, and strongly corroborates the conclusions we have arrived at.

In the course of the year 1860, a very extensive chemical manufacturer consulted one of us respecting his leaden chambers, one of which had been in use for fifteen years, and remained apparently in good condition, whilst another, less than one year old, was attacked on all sides, its interior being furrowed with fissures. Having taken a piece of lead from the sound chamber (No. 1) and two samples from the injured one, the first (No. 2) from a part still uninjured, and the second (No. 3) from a place attacked by the acid, we submitted these samples to analysis, and were surprised at the following results:—

	1.	2.	3.
Lead . . .	98·87	99·37	99·45
Tin . . .	0·91	traces	traces
Iron . . .	0·12	0·37	0·32
Copper } Zinc } .	traces	0·16	0·17
	99·90	99·90	99·94

These figures show that the chamber which had so long resisted the action of the acid was made of lead differently or more largely

alloyed than that of which the other chamber was made. The question then arose which we have endeavoured to answer in this paper.

There is yet another question to be solved, viz., which metal is it that, mixed with lead, enables it to resist the action of sulphuric acid, and in what proportions should that metal exist in the mixture? Is it, as the foregoing analysis would appear to indicate, tin? We hope, at a future date, to be in a position to answer this question.

XI.—*On Formamide.*

By A. W. Hofmann.

As a link of connection between Mineral Chemistry, and what is generally called Organic Chemistry, the formyl series has always been particularly interesting to chemists, and it is therefore surprising that it should still present so many gaps. To those engaged in teaching, this incompleteness is often very embarrassing, as it compels them to borrow the wanting terms from more elaborated groups, or to commence the development of the chemistry of carbon from the second instead of the first step of the ladder. In treating of formate of ammonium and its derivatives, who has not felt the inconvenience of not being permitted to speak about formamide, the existence of which, nevertheless, no one could have possibly doubted?

We know, from the experiments of M. Pelouze,* that hydrocyanic acid, assimilating two equivalents of water, is converted into formic acid and ammonia. In showing that formate of ammonium, when submitted to the action of heat, is transformed again into water and hydrocyanic acid, the same chemist pointed out, for the first time, a re-action, which subsequently, in the hands of MM. Dumas, Malaguti, and Leblanc,† has furnished such memorable results. Half-way between formate of ammonium and hydrocyanic acid, theory justifies us in searching for formamide.

* Pelouze, Ann. Ch. Phys. [2] xlviii. 395.

† Dumas, Malaguti, and Leblanc, Compt. rend. xxv. 383, 442, and 474.

Formate of ammonium $CH(H_4N)O_2$

Formate of ammonium $CH(H_4N)O_2 - H_2O = CH_3NO$ Formamide.

Formate of ammonium $CH(H_4N)O_2 - 2H_2O = CHN$ Hydrocyanic acid.

But if we consult the Manuals of Chemistry, we look in vain for an account of this substance; we are in fact told that the reactions, by means of which we might expect most readily to obtain it, fail to yield the desired result. The simplest process which suggests itself for the preparation of formamide, would appear to be the action of ammonia upon formic ether. But, according to Gerhardt,* who does not state the authority,† dry ammonia does not act upon formate of ethyl; and aqueous ammonia, like the other caustic alkalies, transforms it into alcohol and alkaline formate.

On repeating this experiment, I have, perhaps by changing the mode of operation, arrived at different results. Dry formate of ethyl, saturated with dry ammonia, was exposed in sealed tubes for two days to the temperature of boiling water. On submitting the product of digestion to ebullition, a large quantity of formate of ethyl, which, on account of the small proportion of ammonia soluble in the ether, had remained unchanged, passed over; the boiling point then rose rapidly to 195°, when a transparent, colourless liquid distilled over, not without partial decomposition. This substance, which is equally soluble in water, alcohol and ether is *formamide*.

0·5173 grm. of substance gave 0·5172 grm. of carbonic acid, and 2·122 grm. of water.

The formula—

$$CH_3NO = \left.\begin{matrix}(CHO)\\H\\H\end{matrix}\right\} N$$

requires—

		Theory.	Experiment.
C	= 12	26·66	27·61
H_3	= 3	6·66	6·71
N	= 14	31·12	—
O	= 16	35·56	—
	45	100·00	

* Gerhardt, Traité, i. p. 235.

† Gmelin (*Handbook*, English Edition, vii. 483) gives the same statement on the authority of Liebig.

Rapidly distilled by itself, formamide splits in a great measure into carbonic oxide and ammonia, the two gases being evolved in torrents during ebullition:

$$CH_3NO = CO + NH_3.$$

This decomposition has prevented a very accurate determination of the boiling point, which lies between 192° and 195°. In a partial vacuum, which reduces the boiling point to 140°, formamide may be distilled without the slightest decomposition. Treatment with acids and alkalies converts this substance into formic acid and ammonia. When distilled with anhydrous phosphoric acid, the new amide is converted into hydrocyanic acid. Formamide appears to exist, at the common temperature at all events, in the liquid condition only. Although I have carefully dried it, and kept it for several weeks over sulphuric acid, I have not been able to observe any tendency to crystallisation.

XII.—*Note on the Bicarbonate of Ammonia of the Chinca Isles.*

By T. L. Phipson, Ph.D., F.C.S., &c.

The Chinca isles, which lie off the Coast of Peru, consist of three small rocks, the greater portion of their surface being covered with layers of guano, varying in thickness from ten to thirty yards. Here and there only the naked rock is laid bare. The quantity of guano lying in 1861–62 upon these little islands was estimated at 24,000,000 tons. Underneath the guano is found a comparatively thin layer of a white substance, forming beds several inches thick, and consisting chiefly of bicarbonate of ammonia. This salt has been met with also in Patagonia and Africa. The only mention I have found of this substance, as a natural production, is in Dana's excellent treatise on mineralogy, where he gives for its composition, NH_4O 32·91, CO_2 55·69, HO 11·40 = 100. But this applies only to the chemically pure bicarbonate, and appears to be simply a calculated result, as the natural substance is never quite pure. I am indebted to Captain Marcus Lowther, R.N., for a very fair specimen of this natural carbonate, which that gentleman procured whilst at the Chinca

isles. It is white, crystalline, compact, fragile, having an odour of ammonia, soluble in water, almost entirely volatilised by heat. Its composition, according to my analysis, is as follows:—

		Atomic ratio.	
Ammonia, NH_4O . .	29·76	1·144	1
Lime	6·02	0 215	
Magnesia . . .	traces		
Water	11·00	1·222	1
Carbonic acid. . .	51·53	2·342	2
Sulphuric acid, Chlorine . .	traces		
Phosphoric acid . .	0·60		
Uric acid, Alkalies . . .	1·09		
	100·00		

This agrees nearly with the formula $NH_4O,2CO_2,HO$ (which is that of the artificial bicarbonate of ammonia) for five equivalents of which there is in this specimen one equivalent of carbonate of lime. This natural substance differs from the scentless bicarbonate of the laboratory, by having a tolerably strong smell of ammonia, which proves that it contains a small quantity of free ammonia, or of sesquicarbonate, and accounts for the slight difference between the analytical result and the theoretical formula.

It appears quite evident that this bicarbonate of ammonia results from the decomposition of the guano which it underlies, whilst, on the other hand, guano gives birth to another substance, known in commerce as "West India Phosphate," &c., which possesses the colour and aspect of guano, but contains only about 0·5 *per cent.* of nitrogen, with abundance of phosphate and carbonate of lime. An analysis of this other product of the decomposition of guano has given me:—

Moisture	1·0
Organic matter containing 0·46 of azote .	16·5
Phosphate of lime	35·5
Carbonate of lime	34·0
Sand	12·0
Sulphate of lime, &c.	1·0
	100·0

This substance has the aspect of guano; it has no smell and contains no nodules.

It contains not a trace of uric acid, but a notable amount of xanthic oxide, which can be isolated by boiling the substance with a dilute solution of caustic soda, and passing a current of carbonic acid through the filtered liquid. In this manner, the xanthic oxide $C_5H_2N_2O_2$ is thrown down as a very fine yellowish-white powder, which can be collected on a filter, though it remains a long time suspended in the liquid. It presents all the characters of the xanthic oxide discovered by Dr. Marcet. Xanthic oxide appears to have been met with before in some kinds of guano, but it differs notably from the basic principle, guanine, discovered by M. Unger.

From the above it may inferred that guano is capable of splitting up, by gradual decomposition, into a *mineral* portion containing phosphate and carbonate of lime, and an *organic* portion consisting entirely of bicarbonate of ammonia. But when we compare the quantity of carbonate of lime (34 per cent.) in the former product, with that contained in the rock, sombrerite* (5 per cent.), we cannot attribute the formation of the latter mineral to ancient deposits of guano; moreover, sombrerite contains at least 17 per cent. of phosphate of alumina,—an ingredient never present in guano.

XIII.—*On the Formation of Phenic and Benzoic Acids from Benzol.*

By A. H. Church, B.A., Oxon.

In the summer of 1862, I brought before the notice of the Society some experiments, then in progress, as to the action of sodium-amalgam upon the chloride of phenyl derived from benzol; the object of my enquiry being the isolation of the radicle, phenyl. But Fittig† had already obtained this substance in a pure state: for a repetition of Fittig's experiments has convinced me that the discovery of the true phenyl was the reward of his labours. I have, therefore, relinquished the further prosecution of my own inquiries in this direction, and have now merely to record one or

* See Journal of the Chemical Society, 1862, p. 277.

† Annalen der Chemie und Pharmacie, cxxi, 361. (March, 1862.)

two interesting transformations observed during the course of my experiments with chloride of phenyl.

Chloride of phenyl obtained, as I suggested,* by the action of nascent chlorine upon benzol, is identical in every point examined with the substance derived from phenic acid by the action of pentachloride of phosphorus. If the crude product of the former reaction be washed with strong aqueous potash, and rectified once or twice, a large quantity of pure chloride of phenyl, boiling at 136° C., may be readily procured. When this liquid is distilled from sodium-amalgam, a volatile liquid is produced, in which I erroneously imagined phenyl should be found, while, in fact, this substance is to be sought for in the more fixed residue of the reaction. In this residual mass (besides phenyl $C_{12}H_{10}$, boiling at 245°, and fusing at 70·5°) traces of a bright yellow crystalline matter occur, apparently identical with chrysene (n C_6H_4), and possibly polymeric with phenylene, the olefiant of the series. But among the volatile products of the reaction, besides a large proportion of benzol, and traces of other bodies not yet sufficiently investigated, a small quantity of a hydrocarbon is found boiling at or near 91° C., and having the empirical formula C_6H_4,—a formula which a determination of the vapour-density of a specimen purified as far as possible from benzol, tended to confirm. The insufficient amount of this bye-product, and the great difficulty of purifying it without almost entire loss, precluded further and more exact determinations of its constitution and relations.

If, instead of using aqueous potash in purifying the crude chlorinated benzol (which mainly consists of C_6H_5Cl,HCl), strong warm alcoholic potash be employed, an energetic reaction is set up, and a far more profound transformation is effected, in accordance with the equation—

$$C_6H_5Cl + KHO = KCl + C_6H_5HO.$$

The body C_6H_5HO thus formed, is, when purified and dried, undistinguishable in any respect from ordinary crystalline carbolic or phenic acid, boiling at 186° to 187° C.; having the same specific gravity, 1·068, and the same solubility in water about 1 in 25. It was separated from the hot alcoholic potash-solution by the addition of hydrochloric acid. After fractional distillation, the portion

* Chem. News, Dec., 1859.

collected between 185° and 190° C., was combined with soda to separate any traces of hydrocarbons or unchanged chloride of phenyl, and the phenate of sodium then decomposed with hydrochloric acid. The phenic acid was syphoned off and shaken with a quantity of water insufficient completely to dissolve it. To the filtered aqueous solution was then added common salt in excess; the phenic acid thus separated, when dried by means of chloride of calcium, was absolutely pure. I am aware that Laurent and Gerhardt (in 1849) obtained phenic acid by boiling with strong potash-solution the crude product obtained by acting on phenic acid with pentachloride of phosphorus. But they did not operate upon pure chloride of phenyl (for they could not distil their product without change), and they did not take benzol as their starting point, as I have done in my experiments.

The phenic acid obtained from benzol readily combines with sulphuric acid to form phenylsulphuric acid $C_6H_5HSO_4$. Saturated with carbonate of barium, this acid yielded the barium-salt, $C_6H_5BaSO_4$ at 115° C. This compound perfectly dry, if mixed with half its weight of cyanide of barium and strongly heated, yields, together with benzol, phenic acid, and other products, unmistakable traces of cyanide of phenyl or benzonitrile. A sufficient quantity of this last substance was obtained and isolated for identification in several ways. Ebullition with potash yielded with this product, ammonia and benzoate of potassium. The benzoic acid thus obtained was found to fuse, like ordinary benzoic acid, at 119°—120° C.; a gramme dissolved in bisulphide of carbon, and treated with pentachloride of phosphorus, yielded ordinary chloride of benzoyl, from which ordinary benzoic aldehyde was made; heated with ethylsulphuric acid, it yielded the characteristic odour of ordinary benzoic ether. Its crystalline form appeared identical with that of the normal acid. The point of ebullition of the nitrile seemed to lie at or near 190° C. The reaction by which it was formed should be expressed by the equation—

$$\left.\begin{matrix}C_6H_5\\Ba\end{matrix}\right\}SO_4 + BaCN = \left.\begin{matrix}Ba\\Ba\end{matrix}\right\}SO_4 + C_6H_5CN$$

but other changes very greatly preponderate.

The near relation of benzol to phenic acid, as indicated by these experiments, is not an unreasonable one when we consider how very frequently these two bodies occur together in the products of

destructive distillation; nor is the connection of the phenyl-series with that of benzoyl more unlikely when we recollect Dr. Hofmann's success in obtaining benzonitrile (and consequently benzoic acid) from phenylamine by passing it through a red-hot tube: the same chemist's production of ordinary benzoic acid from toluol (a result confirmed by Schwanert); and Abel's oxidation of cumol into the same substance.

Fittig observes, not apparently from observations of his own, that the bromide of phenyl from phenic acid yields benzol, not phenyl, when decomposed by sodium. Yet my own results with the chloride derived from benzol show that the regeneration of the original hydrocarbon may occur under the same conditions as those which furnished M. Fittig with the means of obtaining phenyl. In that chemist's experiments, a bromide of phenyl was used. It was formed by the spontaneous action of 2 eqs. of bromine upon 1 eq. of benzol, and was found to boil at 152° C.

XIV.—*Analysis of Red Chalk.*

By A. H. Church, B.A.

The late Mr. H. Styleman le Strange, of Hunstanton Hall, Norfolk, whose recent loss science as well as art has to deplore, placed in my hands for analysis and experiment, several specimens of Red Chalk from his estate. Some of these specimens were excessively hard, so much so that they were difficult to crush, even in the iron mortar; others had the consistence of the softest iron-ochres. They varied, too, in depth of tint, from a fawn colour to the deepest brick-red, some being almost as bright as a mixture of equal weights of vermilion and Venetian red. It was impossible to expect concordant results from the analysis of such diverse samples, yet I hoped that a careful examination of this interesting, though variable substance, might throw some light upon its origin. The hard nodules contained as much as from 31·2 to 36·9 per cent. of anhydrous sesquioxide of iron, while the

pale red varieties, not harder than common white chalk, contained no more than from 12·73 to 4·1 per cent. My analyses were made in March, 1862, and the specimens had been procured from Hunstanton in the preceding month. The large quantity of water which they contained is therefore perhaps to be explained from the season of the year in which they were collected. But I found that a portion of this water was so intimately combined, that an exposure of the finely powdered chalk to the temperature at which tin melts, during two hours, was insufficient to remove it at all. My attention was directed to this point more particularly by an analysis of red chalk made last summer, and quite recently published,* by Mr. R. Calvert Clapham. He finds no water whatever in the specimen analysed, although his other numbers agree, for the most part, with some at all events, of those which my determinations have given me. I quote his analyses of red and white chalk below:—

	Red Chalk.	White Chalk.
Carbonate of calcium	80·04	95·80
Sulphate of calcium	0·10	trace
Sesquioxide of iron.....	9·60	1·08
Alumina	1·42	0·52
Magnesia.....	0	0·48
Silica	9·28	2·28
Manganese	trace	0·11
	100·44	100·27

It is impossible to conclude from these results, that the iron-compound present in red chalk was derived from the oxidation of iron pyrites: for not only is there an almost complete absence of sulphate of calcium from the red chalk itself, but, as I shall show, a spring in the neighbourhood of this stratum, and percolating through it, contains nothing more than a minute trace of sulphate in the gallon. I have never detected as much as 2· per cent. of sulphate of calcium in the red chalk examined, as will be seen by the following analyses, one of which includes all the chief constituents of this mineral, while the others refer only to the sulphate of calcium, the carbonate of calcium, and the sesquioxide of iron.

* Chem. News. vol. vi., Dec. 27, 1862.

	I.	II.	III.
Carbonate of calcium	44·75	50·07	65.03
Sesquioxide of iron	36·90	31·20	12·73
Alumina	0·18	not determined.	
Silica	0·72	not determined.	2·21
Sulphate of calcium	0·04	·075	0·15
Carbonate of magnesium	0·35	not determined.	
Manganese	trace		
Chloride of sodium	0·03		
Water	16·41		
Other substances and loss	0·62		
	100·00		

Analyses I. and II. were of the hard dark nodules; III. of one of the softer bright red massive varieties. No specimen analysed contained more than 2·25 per cent. of silica. This fact, and the minute proportion of alumina present, seem to preclude the idea entertained by Professor Phillips, that the iron-oxide owes its presence in the chalk to the decomposition of glauconite or augite.

The chalybeate water of Barrett Ringstead, 1½ miles from the coast, which, at least, percolates through the red chalk,—though it contains 25·05 grains of solid matter per imperial gallon, of which 16·155 grains are carbonate of calcium, 9·74 grains carbonate of magnesium, and 0·913 grain protocarbonate of iron, hardly yields a weighable quantity of sulphate of barium, when to an imperial gallon of the water, evaporated to a small bulk, chloride of barium is added.

When a specimen of red chalk tolerably rich in iron-oxide, is finely powdered and strongly ignited, it offers a remarkable change of colour, becoming of a dull sage-green. But if the iron-oxide exists in larger proportion as compared with the carbonate of calcium than about 4 to 9, then the colour is brownish and the green tint is not apparent. This observation, taken in connection with the fact that the green substance resulting from the ignition of the sesquioxide with chalk can scarcely be made to re-absorb any of the carbonic acid it has lost during the process, has led me to the conclusion that a ferrite of calcium is produced under these circumstances,—while the results of some synthetical experiments on the subject, induces me to suggest the formula—

$$3Ca_2O, Fe_4O_3$$

for the salt thus formed.

XV.—*On Perchloric Acid and its Hydrates.*

By Henry Enfield Roscoe, B.A., Ph.D.

(Abstracted from the Proceedings of the Royal Society, xi, 493.)

Stadion,* in the year 1816, showed that perchlorate of potassium contains 45·92 per cent. of oxygen, and that its composition is therefore represented by the formula ClO_4K (requiring 46·17 per cent. of oxygen). Mitscherlich† and Serullas‡ in 1830, and Marignac§ in 1841, confirmed this result, their experiments respectively showing that the salt in question contains 46·06, 46·20, and 46·17 per cent. of oxygen.

Upon these determinations is based nearly all the knowledge we possess of the quantitative relations of perchloric acid. The anhydride, Cl_2O_7, has not been isolated; no analyses of the hydrated acid itself have been published, and the composition of only one or two of its salts has been ascertained. Our acquaintance even with the general characters of this substance is also most limited; and we can only account for the neglect with which chemists have treated the highest and yet the most stable of the oxides of chlorine by the fact that the preparation of the acid in large quantity has hitherto been attended with great difficulties.

The following communication contains the results of experiments which I believe somewhat enlarge our views respecting the nature and properties of this interesting acid.

The first point to which attention was naturally directed, was the best mode of preparing the pure aqueous perchloric acid in quantity. After trial of a great number of methods, the following modification of that recommended by Serullas was adopted as yielding the best results. A large quantity of a saturated solution of hydrofluosilicic acid was prepared by heating dry sand and fluor-spar with more than the equivalent quantity of twice-rectified oil of vitriol in large stoneware bottles, and leading the gaseous fluoride of silicon with the usual precautions, into water. After straining off the precipitated silica, the acid was boiled down with chlorate of potassiun (not perchlorate, as Serullas advises), added in such quantity that for every kilogramme of fluor-spar 600 grammes of

* Gilbert's Annalen, lii, p. 197 and 339.
† Pogg. Ann., xxv, p. 287.
‡ Ann. Ch. Phys., xlv, p. 270.
§ Ann. Ch. Pharm., xliv, p. 11.

chlorate was present. On heating the mixture, the liberated chloric acid undergoes quiet decomposition, chloric oxide, and probably other oxygen compounds of chlorine, escaping as gas, whilst aqueous perchloric acid remains in the liquid. After the mixture has cooled, the aqueous acid was decanted from the insoluble fluosilicate of potassium, and the clear liquid concentrated by boiling until the perchloric acid began to volatilize. The acid was them distilled, and freed from chlorine by perchlorate of silver, and from sulphuric acid by perchlorate of barium. According to this method, 4 kilogs. of chlorate of potassium yielded 500 grammes of pure concentrated aqueous perchloric acid.

The aqueous acid thus prepared is a colourless, heavy, oily liquid, in appearance undistinguishable from oil of vitriol: its composition and properties will be hereafter described.

From this substance I have succeeded in preparing two definite compounds. One of these is the liquid pure perchloric acid, $Cl\Theta_4H$, an interesting body which was previously unknown; and the other is the monohydrated or crystallized acid, $Cl\Theta_4H + H_2\Theta$, originally discovered by Serullas, but obtained by him in such small quantities that he was unable to determine its composition.

If aqueous perchloric acid be distilled with four times its volume of oil of vitriol containing 98·5 per cent. of real acid, decomposition begins at a temperature of about 110° C.; dense white fumes are evolved and escape, whilst a yellowish, mobile, easily condensable liquid is found in the receiver. If the distillation be continued, the temperature gradually rises to 200° C., and a thick oily liquid distils over, which, on coming into contact with the more volatile liquid in the receiver, immediately unites with it, forming a white, solid, crystalline mass. Both the first and the last portions of the distillate thus prepared, were found to contain sulphuric acid mechanically carried over, and were therefore unfit for analysis. In order to obtain the substances in a pure state, the crystallised acid thus prepared requires redistillation. Heated, however, to a temperature of 100° C., the crystals themselves undergo a decomposition similar to that just described, a strongly fuming volatile liquid first distilling over, and the oily acid appearing in the neck of the retort when the temperature rises to 203° C., and producing crystals on coming in contact with the first distillate. These crystals are likewise formed when water is added to the volatile liquid; and this is, in fact, the best mode of preparing them in the pure state.

1. *Perchloric Acid,* ClO_4H.

Pure perchloric acid may be obtained in quantity by the process above described, or, more easily, according to the following method: — Perchlorate of potassium is distilled together with four equivalents of strong sulphuric acid, until the drops of distillate no longer solidify on falling into the receiver; in this way 100 grammes of perchlorate yield 14 grammes of crystallised perchloric acid containing traces of sulphuric acid. The impure crystals are then melted, placed in a small bulb-retort, and gently heated. Ebullition commences at 110° C., and the decomposition continues for some time without further aid of heat; dense white fumes, accompanied by small quantities of chlorine, issue from the mouth of the apparatus, and a mobile, easily condensable, heavy liquid is found in the receiver. This liquid is pure perchloric acid, ClO_4H, which, if the distillation has been conducted slowly, is perfectly colourless, but often has a slightly yellow colour, owing to the presence of lower oxides of chlorine. As soon as the first appearance of crystals in the neck of the retort is noticed, the distillation is stopped. The liquid distillate should then be at once sealed up in a bulb with long capillary ends, out of which any wished-for quantity may be obtained at pleasure. The greatest care is necessary in working with this body, owing to its explosive and corrosive properties.

Perchloric acid is a heavy, colourless, volatile liquid, which does not solidify at temperatures above –35° C. At 15°·5 C. the specific gravity of the liquid was found to be 1·782, as a mean of two determinations. The vapour of perchloric acid is colourless and transparent; but when it is brought into contact with the air, dense masses of white fumes of hydrated acid are given off, owing to rapid absorption of atmospheric moisture. Perchloric acid does not give up its oxygen to metals at the ordinary temperature as readily as nitric acid; but when it is heated with finely divided iron, copper, zinc, &c., the oxides of these metals are formed, with evolution of light and heat; sulphur and phosphorus are likewise at once converted into their highest oxides in presence of this acid. It is, however, when brought into contact with a carbonized material, that the energy of the oxidising action of perchloric acid becomes visible, as a single drop of this substance falling upon charcoal, paper, or wood, causes an explosive combustion which in violence does not fall far short of the detonation produced by the

sudden decomposition of the chloride of nitrogen. On dropping it into ether or alcohol, an explosion occurs violent enough to break in pieces the vessel containing the liquid. This latter decomposition may possibly be owing to the formation of the explosive perchlorate of ethyl.* Perchloric acid likewise combines with the greatest energy with water, causing a loud hissing noise, and forming either the crystallised or the oily acid, according to the relative quantities of water and acid present. In working with this substance, the greatest care must be taken, as one drop falling upon the skin produces powerful cauterisation, and leaves a wound which does not heal for weeks. Like nitric acid, $N\Theta_3H$, which in many respects it closely resembles, perchloric acid cannot be distilled by itself under the ordinary atmospheric pressure without undergoing decomposition. The colourless liquid, when gently heated, begins to decompose at 75° C., the temperature gradually rising to 92°, at which point it remains constant for some time, gives off dense white fumes, and quickly turns to a dark blackish-brown colour, large quantities of a yellow gas having the peculiar sweetish smell of chloric oxide being evolved. After some time, drops of a dark-coloured liquid, resembling bromine in appearance, distil over, the decomposition continuing in the retort; this dark liquid contained 94·77 per cent. of $Cl\Theta_4H$. On continuing the distillation, the decomposition became more rapid, and a sharp explosion occurred; the receiver was broken to fragments, whilst the residual liquid in the retort became colourless, and, on cooling, solidified to a crystalline mass containing 87·76 per cent. of $Cl\Theta_4H$. I propose to investigate the composition and mode of formation of this singular body at a future time; it may possibly prove to be the black explosive substance described by Millon† as produced by the action of organic matter on the so-called chloro-perchloric acid. Perchloric acid likewise undergoes spontaneous decomposition at the ordinary atmospheric temperature, even when not exposed to light. The liquid, which when freshly prepared has a slight yellow colour, changes to a deep brown colour when kept in the dark for a few days; and after the lapse of about a fortnight, the bulbs containing the acid are found to have exploded. Hence it is impossible to preserve pure perchloric acid for any length of time; it must be prepared when required from the crystallised acid.

* Roscoe, Chem. Soc. Quart. Journ., vol. xv, p. 213.

† Ann. Chim. Phys. [3], vii, 333.

2. *Perchloric Monohydrate*, $ClO_4H + H_2O$.

The first hydrate of perchloric acid is the solid crystalline substance discovered by Serullas, and supposed by some chemists to be the anhydride.*

It is best prepared in the pure state by carefully adding water to perchloric acid; great heat is thereby evolved, and the crystals which form on cooling generally possess a slight yellow colour, which rapidly disappears when they are exposed to sunlight.

By partially melting the crystals several times and separating the liquid portions, the residue was obtained in a state fit for analysis; it gave 84·55 and 84·89 p. c. ClO_4H, the formula requiring 84·80 ClO_4H and 15·20 H_2O.

The monohydrate of perchloric acid solidifies at the ordinary temperature to long silky needle-shaped crystals, which fume strongly in the air, most rapidly absorbing moisture, and immediately deliquescing on exposure. Placed in a thin bulb in a water-bath, the liquefied acid was found to freeze between 49°·5 and 50°·0 C., whilst the crystals melted between 50°·0 and 51°·0 C.; hence the melting and freezing points of this substance lie within a few tenths of 50° C. The specific gravity of the liquid monohydrate at 50° C. is 1·811; but the solid acid is considerably heavier, owing to the large contraction which the liquid undergoes on freezing. As already described, the monohydrate splits up on heating into real perchloric acid and a less volatile aqueous acid; it therefore possesses no definite boiling point. Heated to 110° C., the melted crystals enter into rapid decomposition, which, when once commenced, continues for some time, even when the thermometer sinks to 95°; on further application of heat, the liquid becomes of a dark yellowish-brown colour, ebullition continues, and the temperature gradually rises to 203° C., at which point the mercury remains stationary, the colourless oily acid passing over unchanged.

Although not so violent in its action on organic matter as the pure acid, the fused monohydrate, when brought into contact with wood or paper, induces immediate combustion; and when dropped into water, it combines, with a hissing noise, forming the aqueous acid.

* Pelouze et Fremy, Traité de Chimie, "Acide Perchlorique," t. i, p. 418.

3. *Aqueous Perchloric Acid.*

There is certainly no other known acid in which the acid and the hydrates differ so widely from each other in their properties as is the case with perchloric acid,—the acid itself being a strongly fuming, volatile liquid, acting in a most violent manner on organic substances, and closely resembling nitric acid, whilst the monohydrate is a solid crystalline body, and the higher hydrates are oily liquids having high boiling points, being devoid of smell, and in outward appearance bearing a striking analogy to oil of vitriol.

When pure aqueous perchloric acid is concentrated by evaporation until white fumes are evolved, an acid is obtained on distillation which boils at a constant temperature (about 203° C.), and has a constant composition. The strength of such a residual acid was determined by volumetric analysis with a standard solution of soda; it was found to contain 71·6 per cent. $Cl\Theta_4H$.

The residual acid boiling at 203° C. left in the retort after distilling the solid monohydrate was found to possess a composition identical with the foregoing.

As the hydrate having the formula $HCl\Theta_4 + 2(H_2\Theta)$ contains 73·63 per cent. of $HCl\Theta_4$, it is seen that aqueous perchloric acid follows the same general relations respecting composition and boiling point that I have shown hold good for so many aqueous acids;* namely, that the phenomena of constant composition and fixed boiling-point are, in the above cases, dependent mainly upon physical rather than upon chemical attractions. The specific gravity was found to be 1·709 at 11° C.

The reactions of aqueous perchloric acid have been sufficiently studied by other observers.

To the foregoing description of the properties of perchloric acid and its hydrates, I have to add the descriptions and formulæ of a few of the salts of this acid, which have hitherto not been examined. In all the analyses, the perchloric acid was estimated by precipitation as potassium-salt in alcoholic solution, a method which in accuracy is second to few of the most exact modes of quantitative determination.

Perchlorate of Ammonium, $NH_4Cl\Theta_4$.

This compound is one of the very few non-deliquescent salts of perchloric acid. It is anhydrous and isomorphous, as Mitscherlich

* Roscoe, Chem. Soc. Quart. Journ., vol. xiii, p. 146.

has shown with the potassium-salt. Analysis gave 15·43 p. c. $(NH_4)_2O$, the formula requiring 15·32 p. c.

Ammonio-perchlorate of Copper, $(NH_4)_2O$.

This salt is anhydrous, and was obtained in dark-blue crystals, which on exposure to air turn green, but do not deliquesce. It is prepared by dissolving carbonate of copper in dilute perchloric acid, and adding an excess of ammonia. The crystals are readily obtained by pouring a layer of strong alcohol on to the surface of the aqueous solution. The salt is decomposed on boiling the solution, half the ammonia being liberated, and oxide of copper precipitated: this decomposition serves as a mode of determining the constitution of the salt, which must be regarded as $NH_4ClO_4, + NH_4CuO$. Analysis gave 17·00 and 17·17 p. c. Cu, 28·30 $(NH_4)_2O$, 54·73 and 54·21 ClO_4; the formula requires 17·30 Cu, 28·38 $(NH_4)_2O$ and 54·32 ClO_4.

Ferrous Perchlorate, $FeClO_4 + 3H_2O$.

This salt is obtained by dissolving metallic iron in aqueous perchloric acid; it is highly deliquescent, does not lose water at 100° C., and decomposes when heated above that temperature. Analysis gave, as the mean of three experiments, 15·56 p. c. Fe, and 54·53 ClO_4. the formula requiring 15·44 Fe, 54·80 ClO_4, and 29·76 water.

Mercurous Perchlorate, $Hg_2ClO_4 + 3H_2O$.

Mercurous perchlorate is a highly deliquescent salt, obtained by dissolving black oxide of mercury in dilute perchloric acid. It does not lose water either at 100°. or *in vacuo* over sulphuric acid. Analysis gave 56·57 and 56·63 p. c. mercury, the formula requiring 56·58 mercury, 28·25 ClO_4 and 15·27 water.

Perchlorate of Lead, $2(PbClO_4) + 3H_2O$.

Perchlorate of lead is an extremely deliquescent salt; it is best prepared by dissolving carbonate of lead in perchloric acid. The salt may be dried *in vacuo* over sulphuric acid without losing water. Analysis gave 44·82 and 44·74 p. c. Pb, and 42·22 ClO_4, the formula requiring 45·00 Pb, 43·26 ClO_4, and 11·74 water.

XVI.—*On the Composition of some Varieties of Native Copper.*

By F. A. Abel, F.R.S.

In pursuing the examination of a large number of specimens of commercial copper, some of the results of which were described to the Chemical Society in 1861, by Mr. Field and myself,* it was thought that a comparison of the metallic impurities, existing in specimens of native copper, with those found in coppers of commerce, would not be without interest. Four specimens of native copper, from Lake Superior, Chile, and Siberia, have been submitted to analytical examination, with special reference to the metals existing in them, in association with the copper. The following is a brief account of the nature of each particular specimen, and of the results obtained by their analyses:—

I. *Native Copper from Chile.*†—This specimen consisted of a sheet or slab, from $\frac{1}{8}$ to $\frac{1}{4}$ inch in thickness, being the particular kind of native copper known in Chile as *Charqui* copper. The specimen was thinly coated in places, on both sides, with steatite, containing an admixture of chlorite, which exhibited small red-brown spots, here and there, due to a peroxidation of its constituent protoxide of iron. This specimen of copper was remarkably pure; it contained neither antimony, arsenic, gold, tin, nor lead, and only minute traces of silver and bismuth, the latter metal being easily recognisable by application of the qualitative method of examination, described in the paper referred to above.

II. Two specimens of native copper from *Minnesota* (Lake Superior) were examined.

One of these was about half an inch in thickness, and had been detached from a large mass. It appeared, at first sight, to be perfectly massive, exhibiting only a few very small superficial cavities. When the specimen was cut up, it was found to contain a considerable quantity of minute cavities and fissures, distributed throughout the mass. These spaces were filled up with small quantities of a mineral, composed of silicic acid, alumina, and sesquioxide of iron, and one of these cavities, larger than most of the others, was lined with silver, in small aborescent crystals. An

* Chem. Soc., Q. J., xiv, 290.

† For this specimen, and those from Lake Superior, I am indebted to the kindness of Messrs. James and Shakespeare.

average sample of the massive copper from this specimen contained 0·56 per cent. of silver; no trace of any other of the metals enumerated above, could be detected.

The second specimen of *Minnesota* copper consisted of fragments, or nodules, varying in weight from about 3 grains to 400 grains, and presenting a water-worn appearance. One of the larger fragments had a thick vein of silver passing through it, composing about one-third of the entire mass. A few of the fragments had minute quantities of crystallised quartz attached to their surfaces, and most of them exhibited, like the specimen described above, minute cavities, enclosing a white substance composed of silicic acid, alumina, a trace of sesquioxide of iron and magnesia. An average sample of this specimen (the piece rich in silver being omitted) was found to contain 0·002 per cent. of silver, and a trace of lead. No other metallic impurity could be detected in it.

III. The specimen of *Uralian* copper examined, was detached from a mass of native copper of great size, exhibited last year in the Russian Department of the International Exhibition, and described as coming from *Kirghiz District*, Siberia.* The structure of this specimen was of a very interesting description. Calcareous spar, presenting the appearance and friability resulting from exposure to a high temperature, was exhibited in large quantities throughout the copper, which presented, therefore, a honeycombed appearance, being built up of cavities, mostly of rhombohedral form. Some of the walls of these cavities were at least half an inch, others less than one-tenth of an inch in thickness. The calcareous spar contained traces of sesquioxide of iron, and was coloured to a considerable extent with carbonate of copper; here and there small quantities of suboxide of copper were dispersed between its cleavage-surfaces. Between it and the copper was a thin crust of suboxide of copper which, in many places, was beautifully crystalline. Small quantities of sulphate of baryta were found to exist in some parts of the specimen.

A sample of this copper, taken from the thickest portion, was found to contain 0·034 per cent. of silver, 00·11 per cent. of bismuth, a minute trace of lead, and no less than 1·28 per cent. of arsenic.

* I am indebted for this specimen to Mr. George Peterson, Russian Commissioner at the Exhibition.

I take this opportunity to offer a few explanatory words with reference to the last paragraph but one of the paper by Mr. Field and myself, on the analysis of commercial coppers, to which I have already referred. It is there stated, that "lead is of very rare occurrence in *cake* copper, both unrefined and refined." The term "cake copper" was intended to be applied here (as may be seen from the details of the specimens examined), to bar- and blister-copper, and to "best selected" and foreign refined coppers. It has been pointed out to us that this term, as employed by us, may lead to misconceptions, inasmuch as copper, such as is employed in the manufacture of sheet and bolt, is known in commerce as "tough-cake copper," or cake copper. As lead is always employed in the refining of this class of copper, it is obvious that the statement made by us with regard to the non-existence of that metal in "cake copper" could not apply to the copper known as *tough-cake*, which, in our series of results, was represented by specimens of sheet- and bolt-copper, manufactured from it, and to which the second statement in the same paragraph of our paper refers, where lead is spoken of as an almost invariable constituent of this variety of copper.

XVII.—*On the Spontaneous Conversion of Gun-cotton into Pectic and Parapectic Acids.*

By Edward Divers, M.D.

Some years ago I made a quantity of pyroxylin from Swedish filtering-paper, using for the purpose a mixture of nitric and sulphuric acids. It was soluble in ether, and I have full reason for believing was quite free from adhering acid. A small portion of it, which was not required for the object of its preparation, lay in a drawer for a month or two, and was then enclosed in a stoppered bottle, and placed incidentally in a position exposed principally to diffused light, and never to the direct rays of the sun.

On opening the bottle about two years afterwards, there was a rush of gas, and from the bottle becoming immediately full of nitrous fumes, the gas was presumed to be nitric oxide. The stopper was replaced obliquely so as to allow of the escape of any more gas that might be generated. It continued for a long time to give

off the smell of nitrous vapours, and gradually deliquesced into a consistent jelly.

In perhaps a year and a-half after first observing signs of decomposition, I examined the contents of the bottle. The jelly was acid to causticity from the presence of nitric acid. It was translucent, and exhibited no admixture of crystalline matter. It was kneaded and shaken with water in a bottle, and left at rest until it had subsided into a flocculent, gelatinous state. The acid liquor was poured off, and the washing repeated, till the resulting liquors were only feebly acid. The insoluble matter, which had now again become purely gelatinous, was placed on a filter, and the washing renewed, until in a short time the washings would hardly pass through the filter. By leaving it for a few weeks, the water last added gradually passed through, and was quite acid. It precipitated basic acetate of lead, reduced tartrate of copper and potassium, and assumed a clear, pure yellow colour when boiled with potassa.

The matter on the filter had become nearly transparent, and evolved a faint, but distinct and persistent, agreeable odour, like that of a volatile oil. It was acid to test paper. It dried up into a transparent gum-like substance, and resumed its first appearance when soaked in water. It burned without evolving any characteristic odour. It contained no nitrogen. It was not coloured by iodine. It was insoluble in water, though it partially diffused through it so as to be nearly invisible until it slowly subsided.

Weak acids did not dissolve it, but deposited it after agitation in a gelatinous, flocculent state. Minute quantities of caustic alkali caused its immediate solution, with the exception of minute traces, like particles of unaltered cellulose. From this solution it was reprecipitated by acids in a gelatinous state. Alkaline carbonates also dissolved it, but not to so great an extent as did the alkalies themselves. Its alkaline solution boiled became of a clear yellow colour, without any shade of brown, and this proved very persistent on dilution, thus reminding one of a solution of auric chloride. Heated in a water-bath for a long time with weak mineral acids, it mostly dissolved with slight coloration. This liquid reduced the tartrate of copper and potassium. A solution of the jelly in carbonate of sodium, slightly acidified with acetic acid, heated to expel carbonic acid, and treated with ammonia, until it rendered faintly blue reddened litmus, gave the following reactions:—No precipitates with chlorides of barium and calcium,

sulphates of magnesium, zinc, manganese, and their isomorphs. Gelatinous precipitates with baryta and lime waters, soluble in acetic acid. A pale, bluish green precipitate with sulphate of copper, not blackened on boiling. Acetate of lead gave a gelatinous white precipitate increased by ammonia. Stannous chloride gave a gelatinous precipitate, soluble in excess of the precipitant. Mercuric chloride gave no precipitate; mercurous nitrate, a white one. Nitrate of silver gave a white gelatinous precipitate, insoluble in acetic acid, not reduced by boiling, but in appearance gradually so in presence of ammonia. The precipitation with nitrate of silver, gave a loose, slowly subsiding, gelatinous precipitate, increased or altered by addition of the precipitant in a way that rendered the point of saturation very indefinite. Ferric chloride gave a red-brown precipitate, insoluble in acetic acid. The sodium-salt was precipitated by alcohol, and soon adhered to the sides of the vessel in tenacious masses. No crystalline salt of any kind was obtained. Analysis was out of the question, from the small quantity of the substance at command, and from ignorance as to the formation of any definite compound capable of purification. But I think I am fully justified by its properties as detailed above in regarding it as *pectic acid*. I failed in procuring either mucic or oxalic acids from it by the action of nitric acid. However M. Chodnew could not obtain the former acid from pectic acid (Gerhardt, *Chimie organique*, ii, 506). The transformation of the jelly on the filter into a soluble acid, as described above, corresponds to the passage of pectic into metapectic acid.

The very acid washings obtained at the beginning of the investigation were neutralized and precipitated with acetate of lead; the filtrate yielding no material precipitate with basic acetate. The acid liberated by sulphuretted hydrogen was concentrated over a water-bath; but as it began to colour slightly after a time, the evaporation was completed in vacuo. It dried up to a small quantity of a mass devoid of crystalline form. This was insoluble in alcohol, and redissolved by water. Its solution gave no evidence of oxalic acid. Heated with oil of vitriol, it gave off vapours like those evolved in similar circumstances from sucrose, and when black oxide of manganese was added, a strong smell of formic acid was developed. The tartrate of copper and potassium was reduced by it. Its potassium-salt refused to crystallize both from acid and neutral solutions. As stated above, it precipitated acetate of lead. It did not appear to prevent the precipitation of ferric

hydrate by potassa. The quantity of acid in my possession being very small, I was unable to prosecute further experiments. But I think enough was done to establish, so far as our knowledge of parapectic acid admits of, that this was *parapectic acid.* It was not saccharic acid; neither was it tartaric or oxalic acid. Finally its association with a substance like pectic acid serves mutually to confirm the conclusion as to the nature of both substances. It is known that there is formed a deliquescent acid when xyloidin is left for sometime in solution in strong nitric acid which is regarded as saccharic acid. However, I got no evidence of this acid being present in the decomposed pyroxylin. By dissolving gun-cotton in potassa, M. Vankerckhoff stated that he obtained tartaric acid among the products (Gerhardt, *Chimie organique,* ii, 507). I kept this in mind while examining the products of spontaneous decomposition, and obtained no evidence of its presence among them. M. Chodnew (op. cit.) is said to have noticed an odour developed by the action of strong sulphuric acid on pectic acid, resembling hydride of benzoyl. The odour given off by the gelatinous mass, after I had removed the strong nitric acid, had a distantly similar odour to this body, at least resembling it more nearly than any other smell I know. In the Journal of the Chemical Society, xiii. 76, Dr. Hofmann records a case of spontaneous decomposition of gun-cotton, in which the products were oxalic acid and gum. In the present case, I did not obtain the slightest evidence of oxalic acid.

This interesting conversion of cellulose into pectic acid is, I believe, new. M. Sacc (Chem. Gaz. 1849) thought that he had produced it by the action of dilute nitric acid on the woody fibre of the pine (*Abies pectinata*); but Mr. Porter (Chem. Gaz. 1849) afterwards showed, that the substance thus formed, had the properties of cellulose, instead of pectic acid.

XVIII.—*Note on Oxamide.*

By Dr. Attfield, F.C.S., Director of the Laboratory of the Pharmaceutical Society.

Some experiments on the action of solution of peroxide of hydrogen on substances likely to be used in medicine, have recently been made by my friend Mr. Robbins, Pharmaceutical Chemist.

Among these mixtures was one containing only hydrocyanic acid and the peroxide of hydrogen. After ten days or so this liquid was observed to contain a white granular precipitate, the particles of which were found, by the microscope, to be aggregations of minute crystals.

An inspection of the formulæ of the two re-agents led me to suspect the precipitate in question to be oxamide :—

$$HO_2 + HNC_2 = C_2H_2NO_2 \text{ or } N\begin{cases} H \\ H \\ C_2O_2 \end{cases}$$

Or rather,

$$2HO_2 + 2\begin{matrix} H \\ NC_2 \end{matrix}\Big\} = N_2\begin{cases} H_2 \\ H_2 \\ (C_4O_4)'' \end{cases}$$

In confirmation of this view the following re-actions were obtained :—

1. Ebullition with solution of potash gave rise to the formation of ammonia and oxalic acid, which were recognised in the usual way :

$$N_2\begin{cases} H_2 \\ H_2 \\ (C_4O_4)'' \end{cases} + 2\begin{matrix} K \\ H \end{matrix}\Big\} O_2 = 2N\begin{cases} H \\ H \\ H \end{cases} + \begin{matrix} K_2 \\ (C_4O_4)'' \end{matrix}\Big\} O_4$$

2. Heated with sulphuric acid, the substance gave ammonia, carbonic oxide, and carbonic acid ; they were identified by the ordinary tests and equal volumes of the two latter gases were obtained :

$$N_2\begin{cases} H_2 \\ H_2 \\ (C_4O_4)'' \end{cases} + 2\begin{matrix} H \\ SO_2 \end{matrix}\Big\} O_2 + \begin{matrix} H \\ H \end{matrix}\Big\} O_2 = 2\begin{matrix} NH_4 \\ SO_2 \end{matrix}\Big\} O_2 + \begin{matrix} CO \\ CO \end{matrix}\Big\} + \begin{matrix} CO \\ CO \end{matrix}\Big\} O_2.$$

3. Hot hydrochloric acid produced ammonia and oxalic acid, their presence being proved as before :

$$N_2\begin{cases} H_2 \\ H_2 \\ (C_4O_4)'' \end{cases} + 2\begin{matrix} H \\ Cl \end{matrix}\Big\} + 2\begin{matrix} H \\ H \end{matrix}\Big\} O_2 = 2\begin{matrix} NH_4 \\ Cl \end{matrix}\Big\} + \begin{matrix} H_2 \\ (C_4O_4)'' \end{matrix}\Big\} O_4$$

Lastly. The substance was found to be volatile without decomposition, and to yield a crystalline sublimate which, in both general and minute appearance, exactly resembled that of some oxamide that had been prepared in the old manner by reaction of ammonia and oxalic ether.

This formation of oxamide is interesting, as being an exception to the general rule, that amides are derivatives of ammonias, and as affording another illustration of the readiness with which, under some circumstances, radicals, like cyanogen, lose their individuality, their elements undergoing redistribution.

The reaction is not, however, wholly unparalleled. Playfair has recorded the fact, that oxamide is produced on boiling ferrocyanide of potassium with nitric acid. Peroxide of hydrogen and nitric acid may be viewed as bodies containing oxygen in a more or less loose state of combination, and the formation of oxamide when either of them is brought into contact with a cyanogen compound is obviously due to the action of nascent oxygen on hydrocyanic acid in the presence of water:

$$O_2 + \left.\begin{matrix}H\\H\end{matrix}\right\} O_2 + 2\left.\begin{matrix}H\\NC_2\end{matrix}\right\} = N_2\left\{\begin{matrix}H_2\\H_2\\(C_4O_4)''\end{matrix}\right.$$

I have indeed succeeded in producing oxamide by heating a mixture of binoxide of manganese and cyanide of potassium with a small quantity of sulphuric acid:

$$2\left.\begin{matrix}Mn\\O_2\end{matrix}\right\} + 2\left.\begin{matrix}K\\NC_2\end{matrix}\right\} + 4\left.\begin{matrix}H\\SO_2\end{matrix}\right\} O_2 = 2\left.\begin{matrix}Mn\\SO_2\end{matrix}\right\} O_2 + 2\left.\begin{matrix}K\\SO_2\end{matrix}\right\} O_2 + N_2\left\{\begin{matrix}H_2\\H_2\\(C_4O_4)''\end{matrix}\right.$$

This simplicity of formation would not, however, have been suspected had not the peroxide of hydrogen reaction been observed.

I had hoped that the above method of preparing oxamide would have proved a general one for the production of all the oxalic amides, that mere digestion of peroxide of hydrogen with cyanides of radicals other than hydrogen would have given oxamides in which hydrogen would be replaced by those radicals, new oxamides being thus brought to light. But experiments in which peroxide of hydrogen and cyanide of ethyl were brought together under varying conditions of temperature, pressure, etc., indicated that such neutral cyanides are not thus acted on; possibly other oxidising agents may attack them.

Of the amidic derivatives of ammonia oxamide is usually represented to have been the first discovered. It is also worthy of note that it is the first that has been formed without the direct intervention of ammonia.

XIX.—*On the Spectrum of Carbon.*

By Dr. Attfield, F.C.S., Director of the Laboratory of the Pharmaceutical Society.

It is well known that a mixture of coal-gas and air burns with a flame of slight luminosity. When such a flame is prismatically examined, its light is found to consist of four groups of rays of different refrangibility. These rays appear in the field of the instrument as faint yellow, light green, bright blue, and rich violet bands of light.

In 1856, Swan found that the spectrum thus obtained was common to all hydrocarbon flames. He showed that the bands were best seen in an olefiant gas-flame fed with air by a blowpipe jet; measured and recorded their distances from each other; and searched for, but did not find, corresponding dark bands in the solar spectrum. He gave no theory in explanation of their origin.

On recently reading Swan's paper by the light that Professors Bunsen and Kirchhoff have thrown on the subject, I came to the conclusion that these bands must be due to incandescent carbon vapour; that, if so, they must be absent from flames in which carbon is absent, and present in flames in which carbon is present; that they must be observable equally in the flames of the oxide, sulphide, and nitride, as in that of the hydride of carbon; and, finally, that they must be present whether the flame be produced by the chemical force, as in burning jets of the gases in the open air, or by the electric force, as when hermetically sealed tubes of the gases are exposed to the discharge from a powerful induction-coil.

Experiment has fully confirmed the truth of this theory. The following are some of the details of the investigation:—

A mixture of coal-gas (saturated with benzole) and oxygen, was burned at an ordinary platinum oxhydrogen safety-jet. In

this way a small pencil of flame was obtained, which gave, on examination by the spectroscope, a brilliant well-defined spectrum. Its yellow-green band, composed, according to the drawing accompanying Swan's paper, of four lines, I find to contain six; the green band to have five instead of two; the blue five, that is one more than Swan noticed; and the violet, beside being distinctly double, to have a faint hair-line between its two halves. Indeed, in this as in other spectra, the reduction of bands into groups of lines seems simply dependent on the refractive power of the spectroscope, an increased number of prisms causing greater dispersion of the spectrum, and, consequently, a division in a line or band that otherwise would appear to be single.

Having thus reproduced a satisfactory spectrum of the flame of a hydrocarbon, I next turned my attention to that of a nitrocarbon. Cyanide of mercury was heated in a retort, and the cyanogen thus produced cooled and dried by passing over fragments of fused chloride of calcium contained in the neck of the retort. Ignited and examined by the spectroscope, this cyanogen flame gave a splendid series of bands, and these became still more distinct and brilliant on feeding the flame with oxygen by the platinum safety-tube already mentioned. Familiarity with the spectrum of hydrocarbon flames enabled me to detect it in this nitrocarbon light, notwithstanding the presence of the many-lined nitrogen-spectrum.

But to establish the absolute identity of position of the supposed carbon lines, the hydro- and nitro-carbon spectra were simultaneously brought into the field of the spectroscope, one occupying the upper, the other the lower half of the field. This was readily effected after fixing the small prism, usually supplied with spectroscopes, over half of the narrow slit at the farther end of the object-tube of the instrument. The light from the oxy-hydrocarbon flame was now directed up the axis of the tube by reflexion from the little prism, while that from the oxy-nitrocarbon flame passed directly through the uncovered half of the slit. A glance through the eye-tube was sufficient to show that the characteristic lines of the hydrocarbon spectrum were perfectly continued in the nitrocarbon spectrum.

To eliminate possible sources of error due to the presence of air the following arrangements were adopted. A glass tube, into the sides of which platinum wires were fused, was filled with cyanogen, the greater portion of the gas removed by a powerful

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air-pump, and a current of electricity passed between the wires. The light thus obtained furnished a spectrum precisely similar to that of the cyanogen flame burning in air. Another tube, containing a trace of olefiant gas, also gave a spectrum identical with that of a hydrocarbon flame fed internally with oxygen and surrounded by air.

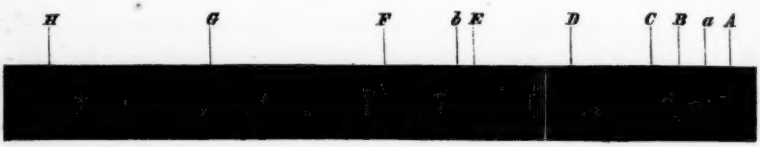
Oxycarbon and sulphocarbon sources of light were then examined. The flames of carbonic oxide and bisulphide of carbon give continuous spectra; even when their combustion is supported by undiluted oxygen, they yield merely furrowed spectra. But when small quantities of them are ignited in tubes, in the manner just mentioned, bright sharp spectra are obtained, and these contain the yellow, green, blue, and violet bands in question, their exact identity, both in nature and position, being in these and in all other experiments proved by the method of interobservation already described.

Having thus demonstrated that dissimilar compounds containing carbon emit, when sufficiently ignited, similar rays of light, I come to the conclusion that those rays are characteristic of ignited carbon vapour, and that the phenomenon they give rise to on being refracted by a prism is the spectrum of carbon.

The spectrum of carbon is a very beautiful one. The lines composing each band of light regularly diminish in brightness in the direction of greatest refraction, and appear to retreat from the observer like pillars of a portico seen in perspective. It differs greatly from that of every other element that I am acquainted with; and though, in each of the experiments described, it was of course accompanied by the spectrum of either nitrogen, hydrogen, sulphur, or oxygen, its diagnosis was not thereby interfered with; it is, in fact, most widely different from, and cannot possibly be confounded with, either of them.

The brightest band of the carbon spectrum being blue, and its other constituents being on the one hand light green and on the other violet, the associated rays of ignited carbon vapour, as indeed seen by the naked eye in carbon flames, I conceive to be of a light-blue colour. The tint may be observed in the flame of a spirit-lamp, in a burning jet of carbonic oxide, in the blowpipe flame of any hydrocarbon, and at the base of a common candle flame. I have no hesitation in saying that should a source of heat be found of sufficient intensity to volatilize the diamond and ignite its vapour, the colour of the light emitted will be blue.

The annexed coloured wood-cut of the carbon spectrum is made on a scale corresponding with that of the spectra, exhibited at page 409, vol. iii, 2nd series, of the Pharmaceutical Journal. The letters refer, as usual, to the prominent dark (Fraunhofer's) lines in the solar spectrum.



XX.—*On the Sources of the Nitrogen of Vegetation; with special reference to the question whether Plants Assimilate Free or Uncombined Nitrogen.*

By J. B. Lawes, F.R.S., F C.S.; J. H. Gilbert, Ph.D., F.R.S., F.C.S.; and Evan Pugh, Ph.D., F.C.S.*

With our present knowledge of the general composition of plants, and of the sources of their constituents, it is easy to see how essential was a proper understanding of the chemistry of the air, and of water, to any true conception of the material changes involved in the vegetative process. It was in fact between 1770 and 1800, that Black, Scheele, Priestly, Lavoisier. Cavendish, and Watt, were engaged in establishing that common air consists chiefly of nitrogen and oxygen, with a little carbonic acid,—that carbonic acid is composed of carbon and oxygen,—and water of hydrogen and oxygen;—and it was within the same period, that Priestly and Ingenhousz, Sennebier and Woodhouse, laboured to show the mutual relations of these bodies and vegetable growth. They seem, however, to have had more prominently in view the question of the influence of plants upon the media with which they were surrounded, than that of the influence of those media in contributing to the increased substance of plants themselves.

Following closely on the footsteps of the above observers, both

* This paper is in the main an abstract of a full report, under the same title in the Philosophical Transactions, part ii, 1861.

in point of time and general plan of research, came De Saussure, whose labours were conducted towards the end of the last, and in the beginning of the present century; and their results together with the arguments founded upon them, were published by him in 1804. To De Saussure we owe the experimental, and even quantative, illustration of the fact, that plants, in sunlight, increase in their amounts of carbon, hydrogen, and oxygen, at the expense of carbonic acid and of water. Indeed, he concluded that air and water contributed a much larger proportion of the dry substance of plants, than did the soils in which they grew.

Besides carbon, hydrogen, and oxygen, plants had already been shown to contain *nitrogen*. Priestly and Ingenhousz thought they had observed that plants absorbed the free nitrogen of the confined atmospheres in which they were placed in their experiments. Sennebier and Woodhouse arrived at an opposite conclusion. De Saussure, again, thought that his experiments indicated rather an evolution of nitrogen at the expense of the substance of the plants, than any assimilation of it from that supplied in the free and gaseous form. In fact, he concluded that the source of the nitrogen of plants was, more probably, the nitrogenous compounds in the soil, and the small amount of ammonia which he demonstrated to exist in the atmosphere.

De Saussure further maintained the essentialness of the incombustible constituents of plants, and pointed out that they were derived from the soil. In his view, the fertile soil was the one which yielded liberally to the plants, nitrogenous compounds, and the incombustible or mineral constituents. He also called attention to the probability that the incombustible or mineral constituents of plants were the source of those found in the animals fed upon them.

Although there still remain to be solved, questions of vast scientific as well as practical interest regarding the conditions under which different plants take up their carbon, hydrogen, and oxygen, yet those who devote themselves to agricultural chemistry soon find that the explanation of the chemical phenomena of agricultural production awaits much more for a further elucidation of the sources, and modes of assimilation, of their *nitrogen*.

In 1837, Boussingault took up the subject of the sources of the nitrogen of plants, where De Saussure had left it more than thirty years before; being apparently led to see the importance of a further investigation of the question by a consideration of the

chemical statistics of certain agricultural practices on the large scale.

To the investigations and conclusions of Bouissingault, and others, reference will be made further on; but before doing so, or entering upon the consideration of our own experimental evidence regarding the assimilation of nitrogen by plants, attention will be called to a few prominent and striking facts established here, at Rothamsted, illustrative of the amounts of nitrogen yielded by different crops over a given area of land, and of the relation of these to certain measured, or known, sources of it.

I.—*Annual yield of Nitrogen per Acre in different Crops.*

The following summary table shows the average annual yield of nitrogen per acre, in the respective crops, when each was grown year after year on the same land, without manure, or with mineral, but without nitrogenous manure.

TABLE I.

Crop.	Seasons.	No. of years.	Nitrogen per acre per annum. lbs.
Wheat.....	1844–1859	16	24·4 without manure.
Barley.....	1852—1859	8	24·7 „ „
Beans	1847—1858	12	47·8 „ „
Meadow-Hay	1856—1862	7	39·7 „ „
Turnips	1845—1852	8	42·0 with mineral manure.

In each case, the land was, in an agricultural sense, exhausted before the commencement of the experiment; that is to say, it would, in ordinary practice, have required manure before growing another crop.

It is seen that, without manure, the two Graminaceous crops (wheat and barley) gave an average of about 24½lbs. nitrogen per acre per annum; the Leguminous crop (beans) nearly twice as much, or 47·8lbs , and the mixed herbage of the meadow-hay, comprising both Graminaceous and Leguminous plants, 39·7lbs. Lastly, the turnips, with mineral, but without nitrogenous manure, gave 42lbs.

In reference to these results it should be stated, that the wheat as yet shows little, if any, but the barley with its more superficial range of roots, more obvious indication of progressive decline in the

annual yield; and at present the meadow land shows no signs of diminution of produce. The yield of the Leguminous crop (beans), on the other hand, has depreciated very considerably, the average annual yield of nitrogen over the first six years being 70lbs., and that over the concluding six years only 26lbs. The turnips again, appeared to have greatly exhausted the immediately available nitrogen in the soil, within the range of collection of the barley plant; for, on barley succeeding the eight mineral-manured turnip crops, the produce was only about three-fourths as much as that obtained, in the same season, where barley was grown the second year in succession without manure, and only about three-fifths as much as where barley was grown as the second crop, of the second course, in a series of entirely unmanured four-course rotation-crops.

It should be further explained, that turnips, grown year after year without manure of any kind, yield, after a few years, only a few cwts. of produce per acre; that purely Graminaceous crops have given very little gain in the annual yield of nitrogen by the use of mineral without nitrogenous manures; but that Leguminous crops, like the turnips just referred to, have given a considerably increased crop, and yield of nitrogen, under the influence of purely mineral manures.

In further illustration of the larger amount of nitrogen yielded over a given area in Leguminous than in Graminaceous crops, the following remarkable results may be cited. Red clover was grown in three out of four consecutive years—the intermediate crop being wheat—all without manure:—

TABLE II.

Season.	Crop.	Nitrogen per acre. lbs.
1st year, 1849.....	Clover	206·8
(2nd year, 1850	Wheat	45·2)
3rd year, 1851	Clover	29·3
4th year, 1852.....	Clover	111·9
Average of the three years' clover....		116·0

All further attempts to grow clover, year after year, on this land, have, however, failed. Neither ammonia-salts, nor organic matters rich in carbon, nor mineral manures, nor mixtures of all,

have availed to restore the clover-yielding capabilities of the land. On the other hand, it should be particularly observed that, after taking 206·8lbs. of nitrogen from an acre in the clover crop of the first year, the wheat crop of the succeeding year was about double that obtained in the same season on a plot which had grown the crop for a series of years without manure, and equal to that obtained where during the same period farm-yard manure had been annually applied.

The following table shows the amount of nitrogen obtained per acre in wheat grown consecutively, in wheat alternated with beans, and in wheat alternated with fallow :—

TABLE III.

Period of Experiment ten years, 1850–9 *inclusive.*

			Nitrogen per acre. (lbs.)	
			Total.	Average annual.
Beans	ten crops consecutively	Without manure	346·9	34·7
		With mineral manure	510·6	51·1
Wheat	without manure	10 crops consecutively	234·0	23·4
		5 crops alternated with fallow	219·3	43·9 or 21·9
Wheat / Beans	without manure	5 crops alternated with beans	225·8	45·2 or 22·6
		5 crops alternated with wheat	244·5	48·9 or 24·5
Wheat / Beans	with mineral manure	5 crops alternated with beans	207·0	41·4 or 20·7
		5 crops alternated with wheat	227 2	45·4 or 22·7

The general result is seen to be, that pretty nearly the same amount of nitrogen was taken from a given area of land in wheat, in ten years, whether ten crops were grown consecutively, five in alternation with fallow, or five in alternation with beans. In fact, the crop of wheat was increased fully as much when it succeeded beans, which *carried off* a large amount of nitrogen, and of mineral matter also, as when it succeeded fallow, which *conserved and increased* the immediately available stores both of nitrogen and of mineral matter. It is also a remarkable fact, that *adding nitrogenous manures* is found to have much the same effect in increasing the produce of the wheat crop.

It will be seen by the illustrations next given, that the experimental results thus far adduced are consistent with those obtained

under circumstances more nearly allied to those of ordinary farm practice.

Taking the results of six separate courses of rotation, Boussingault obtained an average of between one-third and one-half more nitrogen in the produce than had been supplied in manure. His largest yields of nitrogen were in the Leguminous crops; and the cereal crops were the larger, when they next succeeded the removal of the highly nitrogenous Leguminous crops.

In the experiments on this point at Rothamsted, the four-course rotation of turnips, barley, Leguminous crop (or fallow), and wheat, has been followed for twelve years—that is, through three separate courses,—*without manure*,* and the average annual yield of nitrogen per acre was 42·6lbs. The second and third courses gave, however, much less than the first, and hence, a smaller average per annum than that stated for the twelve years; the reduction being due to the falling off in the produce of the turnips, and of the Leguminous crop, whilst that of the barley and wheat has hitherto been fully maintained. The average yield of the twelve years is nearly twice as much as was obtained in wheat or barley, grown year after year, on the same land, without manure; and that of the last eight years even is considerably greater than the amount so obtained. The greatest yield of nitrogen was in the clover, which constituted the Leguminous crop of the first course; and the wheat-crops obtained after this clover, and after the beans in the second and third courses, were about double as much as the average where wheat has been grown succeeding wheat without manure, and about equal to the average obtained by farm-yard manure every year, or when wheat was grown after fallow, or after beans in the experiments last referred to.

The general result is, that, when grown year after year on the same land without manure, Graminaceous crops gave about 24½lbs. of nitrogen per acre per annum, and Leguminous crops much more. Nevertheless, the Graminaceous crop was nearly doubled when preceded by a Leguminous one; and it was also about doubled when preceded by fallow. Lastly, a series of entirely unmanured rotation-crops yielded considerably more nitrogen than the continuously grown unmanured Graminaceous crops.

Further, the highly nitrogenous Leguminous crops were found

* The 16th crop, that is the last crop of the 4th course, is now growing, March, 1863.

to be comparatively little benefited by the direct application of nitrogenous manures in the form of ammonia-salts (though they are more so by nitrates), but considerably by mineral manures; whilst the cereals (wheat and barley), which yield a comparatively small amount of nitrogen, were much increased, both in amount of crop and yield of nitrogen per acre, by nitrogenous, but very little by mineral manures.

But, when the growth of crops (particularly the cereals) is increased by the direct application of nitrogenous manures, the increased yield of nitrogen over a series of years, bears a comparatively small proportion to the amount supplied in manure, as the following results will show:—

TABLE IV.

Crops.	Number of years.	Increased Nitrogen in produce for 100 in Manure.
Wheat.....	6	43·0
Barley.....	6	42·5
Meadow-Hay	7	44·8

Thus, over a period of six years, the increased yield of nitrogen in the wheat crop (compared with that without manure) amounted to 43, and in the barley crop to 42½, per cent. of that supplied in manure; and it should be added, that the remainder does not appear to exist in the soil available for an immediately succeeding crop: for it has frequently been found that when an increased yield of nitrogen has been obtained in the season of application equal to about 40 per cent. of that supplied, the increase in the succeeding year, even with the aid of mineral manures, has only been equal to about one-tenth of the remainder.

In the case of the mixed herbage of the permanent meadow, the increased yield of nitrogen was slightly higher in proportion to that supplied than with the cereals. In Leguminous crops it is found to be even somewhat less; whilst root-crops (turnips) seem to gather up nitrogen in somewhat larger proportion to that supplied.

Let it be assumed that the increased yield of nitrogen approximately represents the proportion of that supplied by manure which is recovered in the crop, and the question arises what becomes of the unrecovered amount?

It may in part be drained away and lost. The nitrogenous

compounds may be transformed within the soil, and their nitrogen, in some form, evaporated; or they may for the most part remain in the soil in some fixed combination, to be yielded up only in the course of a long series of years. Ammonia, or nitrogen in some form, may be given off from the surface of the growing plant. Or there may be simply an unfavourable distribution of the supplied nitrogen within the soil for the immediate crop; and the Leguminous crop, alternating with the Graminaceous one, may gather from a more extended range, and leave a residue, or allow the accumulation, of assimilable nitrogen within the range of collection of the crops which succeed it.

These considerations lead us to the next branch of our subject, namely—

II. *The actual or possible Sources of the Nitrogen of our Crops.*

The following actual or possible sources of the nitrogen of our crops, beyond that supplied in manure, may be enumerated:—

1. The nitrogen in certain constituent minerals of the soil, especially the ferruginous and aluminous, and certain nitrides.

2. The combined nitrogen annually coming down in the aqueous depositions of the atmosphere:—(*a*) as ammonia; (*b*) as nitric acid; (*c*) as organic corpuscles, &c.

3. The accumulation by the soil of combined nitrogen from the atmosphere:—(*a*) by surface absorption aided by moisture; (*b*) by the chemical action of certain mineral constituents of the soil; (*c*) by the chemical action of certain organic compounds in the soil.

4. The formation of ammonia, in the soil or the atmosphere, from free nitrogen (the so-formed ammonia either remaining as such, or being oxidated into nitric acid).

5. The oxidation of free nitrogen:—(*a*) by electric action; (*b*) with common oxygen, in contact with porous and alkaline substances; (*c*) under the influence of ozone, or nascent oxygen; (*d*) under that of evaporation, and combustion, as recently supposed by Schoenbein; ammonia at the same time being formed.

6. The direct absorption of combined nitrogen from the atmosphere by plants themselves.

7. The assimilation of nitrogen by plants.

A very few observations may be offered on each of these actual or possible sources of the nitrogen of vegetation.

(1.) The combined nitrogen of certain of the constituent minerals

from which soils are derived, cannot be considered an adequate source of the nitrogen annually carried off in the vegetable produce of the land.

(2.) The combined nitrogen coming down in the aqueous deposits of rain, hail, snow, mists, fog, and dew, part of which is the return from previously existing generations of plants or animals elsewhere, and part the product of new formation, does undoubtedly contribute materially to the annual yield of nitrogen in our crops; and being a source comparatively easily estimated, it has been the subject of a good deal of experimental investigation; more particularly by Boussingault, Barral, Way, and two of ourselves, and by others on a more limited scale.

The following table shows the amount of nitrogen coming down as ammonia and nitric acid in the total rain, hail, snow, and some of the minor deposits, during the years 1853, 1855, and 1856, here at Rothamsted, the nitric acid being in all cases determined by Mr. Way, and the ammonia in some cases by him, and in others by ourselves.

Table V.

	Nitrogen per acre, per annum, lbs.			
	1853.	1855.	1856.	Mean.
As ammonia.....	5·67	5·86	7·85	6·46
As nitric acid	(not determined.)	0·77	0·73	0·75
Total.....		6·63	8·58	7·21

It is seen that the available combined nitrogen so estimated, is computed to supply but a small proportion of that annually removed from an acre of land in different crops. Nor does it appear, from the results of Boussingault, that the amounts of combined nitrogen deposited by dew are such, that were correction made for the larger proportion so received by the soil, or the vegetation covering it, than was included in our collected and analysed aqueous deposits, any material modification in our approximate estimates would be required.

(3.) The amounts of combined nitrogen accumulated by the soil from the atmosphere, by surface absorption, or chemical action (whether due to restoration or to new formation), probably constitute a considerable proportion of that annually available for vegetation over a given area. Numerous investigations have been

undertaken, by ourselves and others, to determine the capacities for absorption of different soils, or constituents of soils; but, unfortunately, quantitative results obtained in the laboratory do not admit of direct and certain application to the estimation of the amount of combined nitrogen so fixed to a given depth, over a given area, within a given time.

(4 and 5.) The circumstances of the formation of ammonia, or of oxides of nitrogen, from gaseous, dissolved, or nascent nitrogen, are at present the subject of much conflicting statement; the various assumed actions being, as yet, by no means all clearly established qualitatively, and still less quantitatively. Moreover, here again, laboratory results would be difficult of application to the estimation of the probable amount of the nitrogen of vegetation due to such sources. To some of the actions in question further reference will, however, be made.

(6.) There is little of either qualitative or quantitative evidence in reference to the absorption of ammonia, or other compounds of nitrogen, from the air by plants themselves. Some vegetable physiologists, indeed, maintain that the leaves of living plants have not the function of absorption from the atmosphere, but only the converse one of evolution into it. Still, a few observations may be offered in connexion with the point in question.

Ripened cereal crops (wheat or barley) contain 1 part nitrogen to about 30 carbon, and Leguminous crops (beans, &c.) 1 part nitrogen to 15 or fewer of carbon. The atmosphere contains about 1 part carbon as carbonic acid to 10,000 of air; and it may be assumed, for illustration, to contain not more than 1 part nitrogen as ammonia to 12,000,000 of air;* or 1,200 times less nitrogen as ammonia than carbon as carbonic acid.

On these assumptions the ambient atmosphere contains a proportion of nitrogen as ammonia to carbon as carbonic acid, 40 times less than that of nitrogen to carbon in cereal produce, and 80 times (or more) less than that in Leguminous produce.

Hence, in point of *actual quantity merely*, the ammonia in the atmosphere would seem very inadequate to yield nitrogen in a degree corresponding to the yield of carbon by carbonic acid; nor does it appear, from observations hitherto recorded, that the nitrogen existing in the atmosphere, in combination with oxygen, would add much to that existing as ammonia.

* The amounts recorded by different observers range from 20·75 to 0·021 ammonia per million of air.

But water would absorb very much more nitrogen as ammonia, or dissolve very much more as carbonate or bicarbonate of ammonia, than it would of carbon as carbonic acid, under equal circumstances. In illustration, it may be mentioned that water at 60° F. (about 15·5 C.), would, at the normal pressure, absorb about 850 times as much nitrogen in the form of ammonia as carbon in carbonic acid; and, under equal circumstances, very many times more nitrogen as carbonate or bicarbonate of ammonia would be dissolved, than there would be of carbon as carbonic acid absorbed. There would appear to be, then, a compensating quality for the small actual and relative amount of nitrogen as ammonia in the atmosphere, in the greater absorbability, or solubility, of the compounds in which nitrogen exists, than of the carbonic acid in which the carbon is presented. How far the proportion of the nitrogen to the carbon available from the atmosphere in the combined form, may be really thus influenced under the actual conditions of vegetation, is a question, the numerous and intricate bearings of which, we do not profess here to enter upon.

One or two further observations may, however, be made as to the bearing of the actual facts of agricultural production on the point under consideration. Thus, Graminaceous crops certainly depend very materially upon combined nitrogen *within the soil*, but are comparatively independent of carbonic acid yielded by manure in the soil; whilst Leguminous crops are at any rate much less benefited by the direct application of nitrogenous manures, from which it might, perhaps, seem that they were more able to avail themselves of nitrogen supplied in some way by the atmosphere, and possibly by the aid of their green parts. Even should this be the case, it can hardly be to a greater *mere extent of surface above ground*, that the result is to be attributed. Thus, a bean and a wheat crop may yield equal amounts of dry matter per acre, but the bean-produce would contain 2 to 3 times more nitrogen, although approximate measurements show that the wheat plant offers a greater external superficies in relation to a given weight of dry substance, and, therefore, greater still, of course, to a given amount of nitrogen fixed. If, therefore, the bean can in some way assume more nitrogen from atmospheric sources than the wheat crop, the result must be due to *character* and *function*, rather than to mere extent of surface above ground. In connexion with this point it may be observed, more particularly with reference to the crops that are grown for their ripened seed, that

the Leguminous crops, however, generally maintain their green and succulent surface, in relation to a more extended period of the season of active growth, than do the Graminaceous crops.

(7.) *Assimilation of free or uncombined Nitrogen by Plants.*—From the above brief review, it appears that those sources of combined nitrogen to plants which have as yet been quantitatively estimated, are inadequate to account for the amounts obtained in the annual produce of a given area of land beyond that attributable to previous manuring; whilst those which have not yet been quantitatively estimated (if even fully established qualitatively) offer many practical difficulties in the way of any such investigation of them as would afford results directly applicable to our present purpose. It seemed, therefore, desirable to endeavour to settle the question, whether or not that vast storehouse of nitrogen, the atmosphere, in which vegetation is seen to live and flourish, be of any measurable avail to the growing plant, so far as its *uncombined* nitrogen is concerned.

The settlement of this question would indicate the degree of importance to be attached to other points of inquiry. Were it found that plants generally, or some more than others, assimilated free nitrogen, much would be gained towards the explanation of certain chemical facts of agricultural production; it would be established that vegetation had the attribute of effecting chemical combinations with an element the most reluctant to associate itself with other bodies in obedience to laboratory processes, and apt to rid itself of connections once formed in the most violent manner; and we should be able more satisfactorily to account for the large actual amount of combined nitrogen existing and circulating in land and water, in animal and vegetable life, and in the atmosphere.

Moreover, the question of the assimilation of free nitrogen by plants, has, of late years, been submitted to an immense amount of research by numerous experimenters, and from the results very different conclusions have been arrived at. Hence, too, it seems desirable, before entering upon the discussion of our own experimental evidence on the point, to pass in review the methods, results, and conclusions of others, more particularly those of M. Boussingault who questions, and of M. George Ville who affirms, the assimilation of free nitrogen by plants; and as, so far as we are aware, the experiments of these other investigators have as yet been only very briefly noticed in English Scientific Journals,

we propose to give a somewhat fuller account of them than would otherwise have been necessary or appropriate.

III. *The researches of others, on the question of the assimilation of free Nitrogen by Plants, and some allied points.*

De Saussure, and his predecessors, sought to solve the question whether plants assimilate free or uncombined nitrogen, by determining the changes undergone in the composition of limited volumes of air by the vegetation of plants within them. Boussingault pointed out that their methods were not fitted to attain the end in view. The general plan instituted by himself, and adopted with more or less modification in most subsequent researches, was:—

To set seeds or plants, the amount of nitrogen in which was estimated by the analysis of carefully-chosen similar specimens.

To employ soils and water containing either no combined nitrogen, or only known quantities of it.

To allow the access, either of free air (protecting the plants from rain and dust), of a current of air freed by washing from all combined nitrogen, or of a fixed and limited quantity of air, too small to be of any avail so far as its compounds of nitrogen were concerned. And finally—

To determine the amount of combined nitrogen in the plants produced, and in the soil, pot, &c., and, so, to provide the means of estimating the gain or loss of nitrogen during the course of the experiment.

M. Boussingault's Experiments.

The following table gives a summary of the results of M. Boussingault's experiments from 1837—1858, inclusive, on the question of the assimilation of free nitrogen by plants; also a brief reference to the conditions under which the results were obtained:—

TABLE VI.

Summary of the results of M. Boussingault's Experiments.

Plants.	No. of seeds.	Period of growth; weeks.	Notes.	Grammes.				
				Seeds or Plants.	Produce, Dry.	Nitrogen.		
						In seeds (or plants).	In Products.	Gain or loss.
1837: Burnt soil; distilled water; free air; in closed summer-house.*								
Trefoil		8	Fine green, but meagre.	2·000	3·218	0·1100	0·1200	+ 0·0100
Trefoil		13	Much foliage, part withered.	2·000	6·288	0·1140	0 1560	+ 0·0420
Wheat	37	8	Weak and slender.	1·526	2·300	0·0430	0·0400	− 0·0030
Wheat	46	13	Lower leaves dead.	2·018	4·256	0·0570	0·0600	+ 0·0030
1838: Conditions as in 1837.†								
Peas	5	14	Flowers and seed.	1·211	4·821	0·0460	0·1010	+ 0·0550
Trefoil (plants)	3	9	Flowered.	1·117‖	2·754	0·0330	0·0560	+ 0·0230
Oats (plants)	4	7	Ripe seeds.	1·889‖	3·484	0·0590	0·0530	− 0·0060
1851 and '52: Washed and ignited pumice with ashes; distilled water; limited air; under glass shade, with carbonic acid.‡								
Haricot, 1851	1	8	Nascent flowers.	0·780	1·870	0·0349	0·0340	− 0·0009
Oats, 1851	10	8	Small pale leaves.	0·377	0·540	0·0078	0·0067	− 0·0011
Haricot, 1852	1	13	Good growth.	0·530	0·890	0·0210	0·0189	− 0·0021
Haricot, 1852	1	13	Open flowers.	0·618	1·130	0·0245	0·0226	− 0·0019
Oats, 1852	4	11	Ears shooting.	0·139	0·440	0·0031	0·0030	− 0·0001
1853: Prepared pumice, or burnt brick, with ashes; distilled water; limited air, in glass globe, with carbonic acid.‡								
White lupin	2	6	Vigorous growth.	0·825	1·820	0·0480	0·0483	+ 0.0003
Do. do.	6	8	Very fine foliage.	2·202	6·730	0·1282	0·1246	− 0·0036
Do. do.	2	7½	Very vigorous.	0·600	1·950	0·0349	0·0339	− 0·0010
Do. do.	1	6	The finest obtained.	0·343	1 050	0·0200	0·0204	+ 0 0004
Do. do.	2	7	Very active growth.	0·686	1·530	0·0399	0·0397	− 0·0002
Dwarf haricot	1	9	Nascent flowers.	0·792	2·350	0·0354	0·0360	+ 0·0006
Do. do.	1	11	Open flowers.	0·665	2·800	0·0298	0·0277	− 0·0021
Garden cress	3	15	3 grew, flowered and seeded; 10 died.	0·008	0·650	0·0013	0·0013	0·0000
	10			0·026				
White lupins	2	19	2 to grow, 8 as manure; vegetation magnificent.	0·627	5·760	0·1827	0·1697	− 0·0130
	8			2·512				
1854: Prepared pumice with ashes; distilled water; current of washed air, and carbonic acid, in glazed case.§								
Lupin	1	9½	11 leaves, some blackish.	0·337	2·140	0·0196	0·0187	− 0·0009
Dwarf haricot	1	10	Open flowers.	0·720	2·000	0 0322	0·0325	+ 0·0003
Do. do.	1	13½	Ripened seeds.	0 748	2·847	0·0335	0·0341	+ 0·0006
Do. do.	1	15	1 small ripe seed.	0·755	2·240	0·0339	0·0329	− 0·0010
Do. do.	2	14	3 ripe seeds.	1·510	5·150	0·0676	0·0666	− 0·0010
Lupin	1	7	1 to grow, 1 as manure; very fine plant.	0 310	1·730	0·0180	0·0334	− 0·0021
Do.	1			0·300		0·0175		
Cress	42	11	30 grew, 12 as manure; seeded.	0·100	0·533	0·0046	0·0052	+ 0·0006

* Ann. Ch. Phys., [2,] lxvii, (1838.)
† Ibid., lxix.
‡ Ann. Ch. Phys., [3,] xli, (1854.)
§ Ann. Ch. Phys., sér. [3,] xliii, (1855.)
‖ Dry.

TABLE VI *(continued)*.

Plants.	No. of seeds.	Period of growth; weeks.	Notes.	Grammes.				
				Seeds or Plants.	Produce, Dry.	Nitrogen.		
						In seeds (or plants).	In products.	Gain or loss.
1851, '52, '53, and '54: Prepared soil, or pumice with ashes; distilled water; free air, under glazed cage.*								
Haricot (dwarf), 1851 ...	1	15	Flowered and one imperfect seed.	0·780	2·170	0·0349	0·0380	+ 0·0031
Haricot, 1852	1	13	Flowered and a pod.	0·537	2·110	0·0213	0·0238	+ 0·0025
Do. 1853	1	11	7 fine flowers.	0·655	2·720	0·0293	0·0270	− 0·0023
Haricot (dwarf), 1854 ...	1	10	4 fine flowers.	0·710	2·200	0·0318	0·0350	+ 0·0032
Lupin (white), 1853.....	1	13	Very fine, 11 leaves.	0·368	1·585	0·0214	0·0256	+ 0·0042
Do. 1854	1	12	Vigorous throughout.	0·341	1·960	0·0199	0·0229	+ 0·0030
Do. 1854	2	8	8 leaves each.	0·630	2·180	0·0367	0·0387	+ 0·0020
Oats, 1852	4	15	Stems slender, ripe ears.	0·151	0·670	0·0031	0·0041	+ 0·0010
Wheat, 1853	5	15	1 died; others 11 leaves each.	0·293	0·900	0·0064	0·0075	+ 0·0011
Garden cress, 1854	210	8	145 plants, each seeded.	0·500	2·225	0·0259	0·0272	+ 0·0013
1858: Nitrate of potassa as manure.†								
Helianthus.....	2	13	Flowered.	0·116	1·168	0·0144‡	0·0130	− 0·0014
	2	13	Flowered.	0·116	2·120	0·0255‡	0·0245	− 0·0010

In Boussingault's experiments in 1837 and 1838, he grew his plants in burnt soil, watered them with distilled water, allowed free access of air, but kept them protected from rain and dust in a summer house. The tabulated results show that the dry substance of the produce was always much more than, and sometimes several fold that of the seeds sown, or plants planted, indicating, therefore, considerable growth, and consequent gain of carbon, hydrogen, and oxygen. They also show that in the case of the Leguminous plants, trefoil and peas, there was a gain of nitrogen varying from 10 to 55 milligrammes in the several experiments; whilst in that of the Graminaceous ones, wheat and oats, in one instance there was a loss, and in another a gain of 3 milligrammes; and in another a loss of 6 milligrammes of nitrogen.

M. Boussingault's conclusions from the above results were in substance as follow:—That certain plants seem adapted to take up nitrogen in the atmosphere, but that it was a question, under what circumstances, and in what state, the nitrogen was fixed. He submitted—that the nitrogen might enter directly into the

* Ann. Ch. Phys., sér. [3] xliii. (1855).
† Compt. rend., xlvii. (1858).
‡ Nitrogen in seed and nitrate.

organism of the plant, provided its green parts were adapted to fix it; that it might be conveyed into the plant in the aërated water taken up by its roots; that there may exist in the atmosphere an infinitely small amount of ammoniacal vapour. He further suggested, that the gain of nitrogen beyond that supplied in manure, which he had observed in agricultural production, and which he thought came from the atmosphere, might be partly due to nitrate of ammonia produced by electric action and brought down by rain.

In 1851 and 1852, Boussingault confined his plants (in pots) in limited volumes of air under glass shades of about 35 litres' capacity, which rested in lutes of sulphuric acid, with tubes passing under for the supply of carbonic acid and water. Pumice-stone, coarsely powdered, washed, ignited, and cooled over sulphuric acid, served as soil, to which ash, from farm-yard manure and from seed of the kind to be sown, was added. In each year haricots and oats were grown, and the table shows that the haricots increased a good deal in dry substance, and in two out of three cases advanced to flowering, and some of the oats shot forth ears. There was, however, in every case, both with haricots (Leguminous) and oats (Graminaceous), a slight loss of nitrogen, varying from $\frac{1}{10}$th of a milligramme to 2 milligrammes.

In 1853, the enclosing apparatus was a large globe or carboy of white glass, of 70—80 litres' capacity. At the bottom, prepared pumice stone (or burnt brick), and ashes, served as soil, which was watered with distilled water, and then the seeds were sown. The neck of the vessel was then closed with a cork, through a perforation in which a flask of carbonic acid was inverted, whose aperture, opening into the globe, was somewhat contracted. Finally, access of air was excluded by bandages of caoutchouc which rendered the whole apparatus air-tight.

In such apparatus, M. Boussingault made five separate experiments with white lupins, all of which grew more or less luxuriantly, and gained considerably in dry substance; but in no case was there as much as a milligramme of nitrogen gained; in three out of the five cases there was a slight loss, in one instance amounting to ·0036 gramme. Two experiments were made with dwarf haricots, in both of which the gain of dry substance was considerable, and in one nascent, and in the other open flowers were developed; but in one case there was a gain of only ·0006 gramme, and in the other a loss of ·0021 gramme of nitrogen.

In an experiment with garden cress, in which three seeds grew and ten served as manure, abundant seed was produced, but there was neither gain nor loss of nitrogen. Lastly, in an experiment with white lupins, in which two seeds were sown to grow, and eight served as manure, the vegetation was very fine; but there was a loss of ·013 gramme of nitrogen, attributed by Boussingault to free nitrogen given off in the decomposition of the organic matter supplied as manure. In such an apparatus, then, eight experiments were made with Leguminous plants, in most of which there was a loss rather than a gain of nitrogen.

To ascertain whether the limitation of growth in the closed vessels was due to the limitation in the amount of air, Boussingault sowed cress under otherwise equal conditions, but in a good soil, and the result was even more luxuriant growth than in a similar soil in the open air.

In 1854, Boussingault grew a number of pots of plants in a metal-framed glass case of 124 litres' capacity, through which, by means of an aspirator of 500 litres, he passed a current of air, washed first through sulphuric acid and then water. He also supplied carbonic acid, generally equal in amount to from two to three per cent. of the atmosphere of the apparatus; and distilled water was also supplied when needed. Prepared pumice, with ashes, served as soil.

Two pots of lupins, four of haricots, and one of cress, were grown in such an apparatus. The increase in dry substance was in all cases considerable; and in some cases flowers, and in others ripe seeds, were developed. In no case was there a gain of nitrogen amounting to one milligramme; and in four out of the seven there was a slight loss, amounting, in one instance, where a lupin had served as manure, to ·0021 gramme.

Here, then, with a current of air, and with Leguminous plants, in six out of seven experiments, there was, upon the whole, a loss rather than a gain of nitrogen.

In 1851, 1852, 1853, and 1854, contemporaneously with the three series of experiments last described, Boussingault grew plants, so covered with a glazed cage as to exclude rain, or any material amount of dust, but allowing the free access of the external air. Haricots, lupins, oats, wheat, and cress, were so grown. The vegetation was in most cases vigorous. In several cases flowers, and in some seeds, were developed. In only one case was there less combined nitrogen determined in the total products, than was

estimated to be supplied. In the nine other experiments there was a gain of nitrogen indicated, varying from ·001 to ·0042 gramme, which Boussingault attributed to organic corpuscles and ammonia in the atmosphere.

Boussingault considered that, bearing in mind the circumstances of the above experiments, the gain was in no case sufficiently great to justify the conclusion that free nitrogen had been assimilated.

M. Boussingault made various collateral experiments to control or explain his results.

Various substances after being ignited were exposed to the air for two or three days, and then the combined nitrogen in them determined. A kilogramme, respectively, of sand gave 0·5, of powdered brick 0·5, of powdered bone-ash 0·84, and of wood-charcoal 2·9 milligrammes of ammonia.

To estimate the influence of organic corpuscles in the atmosphere, a pot of burnt sand, with ashes, the whole moistened with water, was so arranged under a glazed cage as to allow the free access of air, and, after exposure for two and a half months, small spots of cryptogamic vegetation were visible on the sand, but the whole yielded only 0·74 milligramme of nitrogen.

Ashes, if imperfectly burnt, were found in some cases to contain cyanides, in some ferrocyanides, and in others nitrogen in some other condition.

Boussingault considered that the larger gain of nitrogen indicated in his early experiments in free air (in 1837 and 1838) than in the later ones, was partly due to the comparatively defective methods of analysis at the early date, and partly to the distilled water then used containing some ammonia; for he had since learned, in his analysis of rain and other waters, that the distillate from water containing minute quantities of ammonia, did not come over free from it until about two-fifths of the whole had been drawn off.

To get increased vigour of growth, to avoid the loss of nitrogen apparently due to the evolution of free nitrogen during decomposition when organic matter was used as manure, and to determine whether the nitrogen of nitrates be assimilable by plants, Boussingault has latterly made some experiments in which nitrates were employed as manure.

In 1855, Boussingault grew two pots of helianthus, one without nitrogenous manure, and the other with a small known quan-

tity of nitrate of potassa supplied to the soil; also three pots of cress, one without nitrogenous manure, one with a manured soil, and one to the soil of which nitrate of soda was added. In the experiments with nitrogenous manure there was considerably increased assimilation of carbon, and much more nitrogen assimilated than was supplied by the seeds, but the excess was not equal to that supplied in the nitrate, where it was used.

Lastly, in 1858, Boussingault grew two separate pots of helianthus, using as soil sand and quartz, well washed and ignited, with the addition of nitrate of potass, in one case equal 0·0111, and in the other 0·0222 gramme nitrogen. In the first experiment there was 0·0014, and in the second 0·001 gramme less nitrogen found in the plant, soil, and pot, than was supplied in the seed and nitrate; and Boussingault supposed that nitrate had been decomposed in the soil by the organic matter of the débris of the seeds and the roots, and that nitrogen had been evolved.

From the results of these two experiments with nitrates, Boussingault concluded—that there was no assimilation of free nitrogen; that there was a loss of supplied nitrogen, either from the soil or by the plant; and that the amount of carbon assimilated bore a close relation to that of the nitrogen taken up by the plant.

The result is, then, that in Boussingault's experiments, extending over more than twenty years, and made under very varied conditions, neither with Leguminous plants nor others, did he find any assimilation of free nitrogen.

M. G. Ville's Experiments.

M. G. Ville, of Paris, commenced his investigations on the subject of the assimilation of free nitrogen by plants, in 1849.

He first determined the ammonia in the atmosphere by aspiring large quantities, over periods of several months, through acid. In this way he found the air of Paris to give a mean of 0·0237, and that of its suburbs 0·0211 parts by weight of ammonia to 1,000,000 parts by weight of air.

In M. Ville's experiments on the assimilation of nitrogen by plants, he used specially-made porous flower-pots, washed and ignited sand, sand and brick, or sand and charcoal, as soil, adding to it ashes. For the most part, several pots were enclosed in an iron-framed glazed case of 150 litres (or more) capacity, through

which a current of air, washed or unwashed, was aspirated. Carbonic acid and distilled water were supplied as needed. In some cases ammoniacal gas was passed into the air of the apparatus. In others nitrates, or ammonia-salts, were supplied to the soil, and then the plants had free access of air, only shaded from rain and dust.

The following table summarises the chief results of M. Ville on the question of the assimilation of nitrogen by plants:—

TABLE VII.

Summary of M. G. Ville's Experiments.

Plants.	Period of growth; weeks.	Notes.	Dry substance. Grammes.		Nitrogen.—Grammes.			Nitrogen in products to 1 supplied.
			In seed (or plants).	In produce.	In seed; and air or manure.	In products	Gain or loss.	
1849: Current of unwashed air supplying 0·001 grm.: Nitrogen as Ammonia.*								
Cress	9		0·531	8·733	0·0260	0·1470	0·1210	5·6
Large Lupins	9		0·991	3·506	0·0640	0·0640	0·0000	1·0
Small Lupins	9		0·991	2·565	0·0640	0·0470	− 0·0170	0·7
					0·1550	0·2580	0·1030	1·7
1850: Current of unwashed air supplying 0·0017 grm.: Nitrogen as Ammonia.*								
Colza (plants)	17		0·599	53·761	0·0260	1·0700	1·0440	41·1
Wheat	17		0·682	2·807	0·0160	0·0310	0·0150	1·9
Rye	17		0·617	3·136	0·0130	0·0370	0·0240	2·8
Maize	17		1·488	4·503	0·0290	0·1280	0·0990	4·4
					0·0857	1·2660	1·1803	14·8
1851: Current of washed air.*								
Sunflower	13	95 rudimentary grains.	0·184	25·586	0·0050	0·1570	0·1520	31·4
Tobacco	13		0·084	22·436	0·0040	0·1750	0·1710	43·7
Tobacco	13		0·084	20·780	0·0040	0·1620	0·1580	40·5
1852: Current of washed air.*								
Autumn Colza	37	Flowered.	0·854	27·412	0·0480	0·2260	0·1780	4·7
Spring Wheat	16	47 complete grains.	1·194	12·917	0·0290	0·0650	0·0360	2·2
Sunflower	30	412 rudimentary grains.	0·588	64·090	0·0160	0·4080	0·3920	25·5
Summer Colza	15	much leaf.	3·723	60·408	0·1730	0·5950	0·4220	3·4
Summer Colza	10	much leaf.	1·833	64·786	0·1050	0·7010	0·5960	6·7
1854: Current of washed air (under superintendence of a Commission).†								
Cress	10	Did not thrive.	0·319‡	2·242	0·0099	0·0097	− 0·0002	1·0
Cress	10		0·124‡	6·021	0·0038	0·0530	0·0492	13·9
Cress	10		0·128‡	1·506	0·0039	0·0110	0·0071	2·8

* Recherches Expérimen tales sur la Végétation, par M. Georges Ville. Paris, 1853.
† Compt. rend., 1855.
‡ Not dry.

TABLE VII *(continued)*.

Plants.	Period of growth; weeks.	Notes.	Dry substance. Grammes.		Nitrogen.—Grammes.			Nitrogen in products to 1 supplied.
			In seed (or plants).	In produce.	In seed; and air or manure.	In products.	Gain or loss.	
1854: Current of washed air (closed, under the superintendence of a Commission).*								
Cress	7		0·206§	3 599	0·0063	0·0350	0·0287	5·6
1855 and 1856: In free air; with 0·5 grm.: Nitre = 0·069 Nitrogen.†								
Colza	7		0·027	5·450	0·0700	0·0700‡	0·0000	1·0
Colza	7		0·027	5·140	0·0700	0·0660‡	− 0·0040	0·9
Colza	10		0·027	5·020	0·0700	0·0680‡	− 0·0020	1·0
1855 and 1856: In free air; with 1 grm. Nitre = 0·138 Nitrogen.†								
Colza	9		0·031	7·750	0·1400	0·1970‡	0·0570	1·41
Colza	12		0·031	15·300	0·1400	0·3740‡	0·2340	2·67
Colza	17		0·031	10·770	0·1400	0·2160‡	0·0760	1·54
Colza	18		0·031	22·230	0·1400	0·2500‡	0·1100	1·79
1856: In free air; with 0·792 grm.: Nitre = 0·110 Nitrogen.†								
Wheat	24			26·900	0·1260	0·2180‡	0·0920	1·7
Wheat	24			26·520	0·1260	0·2240‡	0·0980	1·8
1855: In free air; with 1·72 grm.: Nitre = 0·238 Nitrogen.†								
Wheat	26	Gave 84 grains.		37·370	0·2590	0·3080‡	0·0880	1·2
1856: In free air; with 1·765 grm.: Nitre = 0·244 Nitrogen.†								
Wheat	22	Flowered		26·87	0·2650	0·2170‡	− 0·0040	0·8
Wheat	29	Gave 119 grains		41·56	0·2650	0·3503‡	+ 0·1320	1·5

In 1849, M. Ville placed three pots of plants in his apparatus, one of cress, one of large lupins, and one of small lupins; sand was used as soil; and the aspirated air was unwashed. The cress plants gave more than sixteen-fold the dry substance of the seed sown; and about five and a half fold the nitrogen in the seed. The other plants did not gain nitrogen. The total nitrogen in the seed of the three pots was estimated at 0·154 gramme, that in the ammonia of the unwashed air 0·001, and that in the total products was 0·285, showing a gain in the three experiments

* Compt. rend., 1855.
† Recherches Expérimentales sur la Végétation, 1857.
‡ In plants only.
§ Not dry.

of 0·103 gramme, or 1·7 fold that supplied. M. Ville concluded that the cress had assimilated a considerable quantity of free nitrogen.

In 1850 four pots, one of colza, one of wheat, one of rye, and one of maize, were enclosed in the apparatus; and the conditions were the same as in 1849, excepting that the experiment with the colza commenced with young plants instead of seed. The produced colzas gave 40—50 fold the dry substance of the young plants; and the nitrogen also increased more than forty-fold. The other plants also gained, but in less amount and proportion. The total combined nitrogen in the contents of the apparatus was nearly fifteen times that supplied, 1·18 gramme being gained. The conclusion was that a large quantity of free nitrogen had been assimilated.

In 1851 the plants were supplied with a current of air washed free from ammonia. One pot of sun-flower, and two of tobacco (the latter starting from young plants), were grown together in the apparatus, with the conditions otherwise as before. The sun-flowers gave 95 rudimentary grains, but the tobaccos did not flower. The three experiments together gave nearly two hundred fold the original dry matter, and nearly forty fold the original nitrogen, the actual gain in the apparatus being 0·481 gramme.

In 1852 the conditions were as in 1851, and the plants grown were autumn colzas (from plants), spring wheat (from seed), sun-flower (from seed), and summer colzas (from plants). All gave a considerable increase of dry matter; and the total combined nitrogen gained in the apparatus was 1·624 gramme, or 5·3 times as much as was supplied in the original plants and seed.

In each of the years 1850, 1851, and 1852, M. Ville had a duplicate apparatus, with plants similar to those in the experiments above described, to which, however, he supplied ammonia in the atmosphere of the apparatus. These duplicate plants increased much more, both in dry substance and in nitrogen, than the others; but the gain of nitrogen was in no case equal to that supplied as ammonia, and hence, the results have not a direct bearing upon the question of the assimilation of free or uncombined nitrogen.

Up to 1853, inclusive, M. Boussingault had experimented either in free air, with protection from rain and dust, or in fixed and limited air, and, considering the conditions, in neither case was it concluded that free nitrogen had been assimilated.

M. G. Ville's experiments up to the same period, had, on the other hand, indicated an enormous gain of nitrogen. Results so strikingly contradictory, naturally excited great attention; but the fact that M. Boussingault's plants had not been supplied with a *current* of air, and some other circumstances, were alleged to account for the difference in result. In 1854, M. Boussingault commenced experiments with a current of air, the results of which have already been given, and a Commission of members of the Academy of Sciences of France, comprising MM. Dumas, Regnault, Payen, Decaisne, Peligot, and Chevreul, was appointed to superintend a new set of experiments by M. Ville.

M. Ville's experiments under the Commission were conducted at the Muséum d'Histoire Naturelle, Jardin des Plantes, Paris; M. Cloez was appointed to assist him, and M. Chevreul reported on behalf of the Commission in 1855. In one apparatus connected with the aspirator three pots of cress were placed, and in another smaller one (which was not opened during the experiment, as the other frequently was,) one pot of cress was grown. In one pot, in the set of three experiments, there was no gain; in another a gain of 0·0492; and in the third, a gain of 0·0071 gramme of nitrogen. In the permanently closed apparatus there was a gain of 0·0287 gramme nitrogen.

Unfortunately, an element of uncertainty attached to these experiments under the Commission. A quantity of distilled water from the bulk used for watering the plants, was in course of evaporation with oxalic acid under the superintendence of M. Cloez, when he was called away for some days; and when M. Peligot determined the ammonia in the acid residue, and also in that of the water removed from the cases, he found such an excess of ammonia in the water before being used over that in the water removed from the larger case, as more than covered the increase of nitrogen in the experiments. But when new portions of the original water were examined, a different result was obtained; and M. Cloez found that the previous evaporation had, in his absence, gone on by the side of ammoniacal emanations. However, the result with the single pot, in the small apparatus, showed a considerable gain of nitrogen, even supposing the first analysis of the supplied water to be correct.

From the result of the whole inquiry, the Commission announced the following conclusion:—

That the experiment made at the Muséum d'Histoire Naturelle,

by M. Ville, is consistent with the conclusions which he has drawn from his previous labours.

In 1855 and 1856, M. G. Ville conducted experiments in which the plants were allowed to grow in free air, only shaded from rain, and of which the special conditions were, that nitrate of potass in smaller or in larger quantity, or nitrate of potassa and different ammonia-salts, in equivalent quantities as to nitrogen contents, were employed. Artificial soils, with ashes of plants, and distilled water, being used as before.

With a view to these experiments, he devised a method for estimating minute quantities of nitric acid, which was favourably reported upon by M. Pelouze, on behalf of a Commission, composed of MM. Balard, Peligot, and himself.

In 1855 two pots, and in 1856 one pot, of colzas were grown, to each of which 0·5 gramme of nitre was supplied. The dry substance increased about two hundred fold; and analysis showed that the total produce contained almost exactly the same amount of nitrogen as that supplied in the seed and the nitrate. In each of the same years two pots of colzas were grown, to each of which 1 gramme of nitre was supplied. The dry matter of the produce was several hundred times as much as that of the seed sown; and it contained considerably more nitrogen than had been supplied in the seed and nitrate. M. Ville concluded that when, by the larger supply of nitrate, the growth had been extended, free nitrogen was assimilated.

In 1855, a pot of wheat was grown manured with 1·72 gramme of nitrate of potass. Eighty-four grains were produced; and there was more nitrogen in the produce alone, than in the seed and nitrate, and much more when the residue in the soil was taken into account. In 1856, two pots of wheat were sown to each of which 1·765 gramme of nitre was added. The plants of one pot were taken up at the time of flowering, and found to contain almost as much nitrogen as was supplied in the seed and nitrate. Those in the other were left as seed, and gave 119 grains; and the nitrogen in the produce, exclusive of the residue in the soil and pot, was much more than that supplied. Also, in 1856, two pots of wheat were sown without nitrate, and two with 0·792 gramme each. The actual gain of nitrogen was the greater where the nitrate was employed, but the proportion gained, to that supplied, was greater where no nitrate was supplied.

In 1856, experiments were also made, comparing the effects of

nitrates and ammonia-salts, from the results of which it was concluded, that a given amount of nitrogen was more efficacious in the form of nitrate, than in that of ammonia-salts.

In regard to the experiments made in 1855 and 1856, in free air, with nitrates or ammonia-salts supplied, M. Ville remarks that the point at which the supplied nitrogen becomes exhausted is indicated by a lightening of the colour of the leaves, and that it is then that the plants begin to assimilate free nitrogen, to secure which it is necessary that the supply of nitrogen, and the vigour of growth, should reach a certain point, but that the supply should not exceed a certain limit. Further, that the gain of nitrogen in the experiments in question was so great, and the amount before shown to be available from atmospheric ammonia was so small, that the influence of that source may be entirely overlooked. He enumerates the following conclusions :—

1. By means of nitre we may prove, without the aid of an enclosing apparatus, that plants absorb and assimilate the gaseous nitrogen of the atmosphere.

2. Nitre acts by its nitrogen. It is absorbed in the state of nitre.

3. In relation to the amount of nitrogen, nitre is more active than ammonia-salts.

M. Ville also made various collateral experiments.*

Air was passed through an otherwise closed apparatus, in which was placed a vessel containing calcined sand, or calcined sand and decomposing organic matter, but in no case was nitric acid formed; hence, nitrification was not the source of the nitrogen gained by the experimental plants.

Given amounts of organic matter, lupins, gelatine, &c., were mixed with calcined sand, and exposed in an apparatus to a current of air which carried the gaseous products through acid. The determination of the nitrogen remaining in the matrix, and of that absorbed as ammonia by the acid, showed a loss of nitrogen given off in the free state. Somewhat similar experiments were made, in which seeds of wheat were sown in the sand, decomposing organic matter serving as manure. When the growth was allowed to continue long enough, the products contained more nitrogen than the seeds sown and the organic matter; in these cases it could not be said that the nitrogen not received by the plants as

* Recherches Expérimentales sur la Végétation, 1857.

ammonia had been taken up as nascent nitrogen evolved in the decomposition.

The conclusions from the collateral experiments were as follow:—

1. Organic matters in decomposition lose a part of their nitrogen as ammonia, and a part as nitrogen gas.

2. Vegetation does not interfere with the progress of this decomposition.

3. Plants cultivated in a manured soil, give more nitrogen in their produce than the manure yields as ammonia.

4. The excess of nitrogen in the produce has been absorbed as free gaseous nitrogen.

In regard to the explanation of the assimilation of free nitrogen by plants, M. Ville calls attention to the fact, that nascent hydrogen is said to give ammonia, and nascent oxygen nitric acid, with free nitrogen, and he asks,—why should not the nitrogen in the juices of the plant combine with the nascent carbon and oxygen in the leaves? He further refers to the supposition of M. De Luca, that the nitrogen of the air combines with the nascent oxygen given off by the leaves of plants, and to the fact that the juice of some plants (mushrooms) has been observed to ozonize the oxygen of the air, and asks—Is it not probable, then, that the nitrogen dissolved in the juices will submit to the action of the ozonized oxygen with which it is mixed, when we bear in mind that the juices contain alkalies, and penetrate tissues the porosity of which exceeds that of spongy platinum?

Results and conclusions so astonishingly conflicting as those of M. Boussingault and M. G. Ville, have naturally incited others, either to investigate anew, or to seek in the conditions provided in their experiments, for some explanation of the discordance. A brief notice of the labours, or opinions, of these other experimenters or arbitrators, may be here subjoined.

In 1851, M. Mène* made three sets of experiments:—

1. Wheat and peas were, respectively, grown in powdered-glass, in free air, and watered with pure water. The wheat gained nitrogen equal to one-fourth of that in the seed sown, and the carbon, hydrogen, and oxygen, were doubled. The peas doubled the carbon, oxygen, and hydrogen, and trebled the nitrogen of the seed.

2. Lentils, peas, haricots, beans, wheat, rye, and oats, were

* Compt. rend. xxxii.

grown in a sterile matrix under a bell-glass, and supplied with an atmosphere of known composition, and with acetate of ammonia in the soil. The plants gained nitrogen, and the soil lost ammonia, but the nitrogen of the air was not perceptibly affected.

3. This series was similar to the second, but with the nitrogen of the air replaced by hydrogen. The plants flourished, and took up some of the acetate of ammonia.

M. Mène concluded that plants do not appropriate the free nitrogen of the air.

M. Roy, writing in 1854,* supposed that carbonate of ammonia was the chief source of nitrogen to vegetation; that Leguminous plants appropriated it from the atmosphere by their leaves; that Graminaceous plants only took it up in solution by their spongioles; and that free nitrogen was not fixed by the leaves of plants, but when dissolved in water, and taken up by their roots, it could be assimilated. He concluded, that in M. Boussingault's experiments in limited air, there would be but little passage of solution of nitrogen by the roots, and evaporation of water from the leaves, and hence, not the necessary conditions for the assimilation of free nitrogen; but that with M. Ville's rapid current of air it would be otherwise.

In 1850, MM. Cloez and Gratiolet published the results of some experiments with water-plants, from which they concluded, that in the vegetation of such plants, nitrogen is given off from their nitrogenous constituents; that there must be restoration either from free or uncombined nitrogen; and that as their experiments showed ammonia-salts to be injurious to the plants, they probably take up free nitrogen dissolved in water.

In 1855, M. Cloez † published the results of some experiments on nitrification, in which he passed washed air for several months through twenty different combinations of porous, earthy, and alkaline matters. He found nitrates to be formed in notable quantity in calcined brick, or pumice, impregnated with alkaline or earthy carbonates, also in uncalcined brick similarly impregnated; but only traces in chalk, marl, a mixture of kaolin and precipitated carbonate of lime, &c. He considered, therefore, that the porosity of the pots and brick-fragments, the alkalinity of the ashes, the moisture, and the current of air, in M. Ville's experiments, provided the conditions for the formation of nitric acid. He asks, can such formation take place in limited air?

* Compt. rend., xxxix. † Compt. rend., xli.

M. De Luca * aspirated a large quantity of air in the neighbourhood of vegetation, through carded cotton, and then through sulphuric acid to wash it. The washed air then passed over potassium and through a dilute solution of pure potass, when nitrate was formed; but when air in the midst of habitations was operated upon in a similar way the formation of nitric acid was not observed. M. De Luca had found that the oxygen given off by plants in sun-light was in many cases ozonous, and supposed that by its means the nitrogen of the air may be converted into nitric acid, and that thus the nitrogen of the air may be rendered available for assimilation by plants, under the influence of vegetation itself.

In 1855, M. Harting † published some observations, and the results of some experiments, on the question of the assimilation of nitrogen by plants. He attributed a formation of ammonia from the decomposing débris of seeds, &c., and the free nitrogen of the air, in M. Ville's experiments; and he also supposed that nitric acid might be formed by the oxidation of the atmospheric nitrogen. The increase of nitrogen in M. Ville's plants, and of ammonia in the water of the enclosing apparatus, was taken as a proof of such formation of ammonia. He made two sets of experiments, in one of which the plants grew in a limited volume of air, and in the other in a current of air washed free from ammonia, both being arranged with a view to avoid the formation of ammonia. However, the produced plants yielded no more dry matter than was contained in the seeds, and M. Harting considered, therefore, that the determination of the nitrogen was superfluous. The growth evidently stopped when the supplies of the seeds were exhausted. His general conclusions were as follow:—

1. Plants absorb salts of ammonia, and nitrates, by their roots.

2. The nitrogen of the air contributes to the formation of ammonia, and nitrates, in the soil.

3. It is not proved that nitrogen serves directly for the nutrition of plants.

In 1852 and 1853, M. H. M. Chlebodarow made some experiments at Dorpat, under the direction of M. Petzholdt, who reported upon the results.‡ M. Petzholdt assumed that if plants can appropriate the free nitrogen of the air, they will not need

* Compt. rend., 1856.

† Compt. rend., xl. (1855.) ‡ J. pr. Chem., lxv.

ammonia, and that if they take nitrogen from ammonia the supply of it will increase growth. The experiments were made upon barley. In 1852 an ignited yellow sand was used as soil. To one set of plants no ammonia was supplied, to a second carbonate of ammonia was provided in the soil, and to a third it was supplied in the air. The crops with a supply of ammonia gave three times as much produce, and much more nitrogen, than those without it. In 1853, six sets of experiments with barley were made, the soils consisting of an artificial mixture of clay, sand, and felspar decomposed by heating with lime. To one set of three pots, no manure was added; to the second, a small quantity of bone-ash, decomposed by sulphuric acid; and to the third, a larger quantity of the same phosphatic mixture. The three other sets were arranged like the above, and had, in addition, ammonia supplied to the atmosphere in which the plants grew; the experiments, without ammonia, being made in free air, and those with it in an enclosing apparatus. The nitrogen of the crops was very much increased by the aid of the phosphatic manure, and still further by the addition of the ammonia to the atmosphere of the plants. M. Petzholdt considered it difficult to account for the fact of M. Boussingault getting little or no increase of nitrogen in free air, which must have supplied some ammonia, even though rain and dew were excluded.

The results or conclusions of these several arbitrators are seen to be nearly as conflicting as those of M. Boussingault and M. G. Ville themselves, nor are we able to discover, either in the differences of plan, as described by M. Boussingault and M. G. Ville themselves, or in the results and explanations of other experimenters, a satisfactory solution of the difference of result arrived at.

From the chemical characters of nitrogen itself, and from what is known of the chemistry of vegetation in other respects, it would be concluded that plants would not assimilate nitrogen offered to them in the free state. On the other hand, the total amount of actually existing combined nitrogen is very large, and there is an amount of nitrogen periodically available for the vegetation of a given area of land, the source of a considerable proportion of which is, to say the least, not yet quantitatively explained; and, upon the decision finally come to in regard to the question whether or not the assimilation of free nitrogen

by plants, may account for all, or a part of the otherwise unexplained amount, must materially depend the degree of importance to be attached to the further investigation of the other actual or possible sources of nitrogen to plants which have been briefly noticed. It seemed desirable, therefore, that the subject should be submitted to further inquiry, and we now proceed to give a condensed account of our own experimental evidence on the point.

IV.—*Experimental results obtained at Rothamsted in* 1857, 1858, *and* 1859, *on the question of the Assimilation of Free Nitrogen by Plants, and some Allied Points.*

In the treatment of this part of our subject, it is proposed to consider—

1. The conditions required, and plan adopted, in the direct experiments on the question of the assimilation of free nitrogen by plants: embracing those which relate to the requirements and preparation of the soil or matrix, and of the nutriment to be supplied to the plants, the selection of plants and seeds, the atmosphere to be provided, the description of apparatus adopted, and the mode of using it (which should be so arranged as to include all that is necessary for the healthy and vigorous growth of the plants, excepting, in some instances, a full supply of combined nitrogen), and lastly, the question of the analytical methods adopted, and of their competency to serve the purposes of the enquiry.

2. A number of collateral questions having a bearing upon the points at issue: including those of the possible influence of ozone on the supply of combined nitrogen to growing plants, of the action of ozonised air on decomposing organic matter, and porous and alkaline substances, of the evolution of free nitrogen in the decomposition of nitrogenous organic matter, and of the mutual relations of gaseous nitrogen and the nascent hydrogen evolved during the decomposition of organic matter.

3. The results of the direct experiments themselves on the question of the assimilation of free nitrogen by plants.

Conditions required, and plan adopted, in Experiments on the question of the Assimilation of Free Nitrogen by Plants.

So complicated is the constitution of ordinary soils, and so intimately are the nitrogenous compounds existing within them associated with other matters, that it is impossible either to estimate their

nitrogen with sufficient accuracy for our present purpose, or to extract it from the soil without entirely destroying the other conditions of vegetable growth; nor could a natural soil be so imitated by artificial means, as to include all its conditions excepting a supply of combined nitrogen. There exists, however, abundant evidence to show that many of the complicated conditions of an ordinary soil may be entirely dispensed with, so as to bring the examination within our means of investigation, and yet, to retain all the conditions of healthy growth. The experiments of others to which attention has been directed, are sufficiently conclusive on this point, and the results now to be recorded bear similar testimony.

In the experiments of the first year, 1857, two kinds of soil, or matrix, were used; one prepared from an ordinary soil, and the other from volcanic pumice. The latter substance was employed with a view to eliminate certain supposed sources of error which the prepared soil might introduce; but results, to which reference will be made, showed the precaution to be unnecessary, and, in 1858, only prepared soil was used.

A somewhat clayey soil was selected; and, after the large stones had been removed, and the clayey lumps powdered, it was ignited in a large cast-iron muffle, through which a constant current of air passed, until, on removing a portion, and cooling it, it exhibited the red colour due to peroxide of iron, and showed no traces of coaly matter. The mass was then thrown into a large volume of distilled water, which was rendered strongly alkaline by the caustic lime present. After stirring, and being allowed to settle, the fluid was decanted, then fresh water added, and the operation repeated frequently during eight or ten days, until all the soluble matter was removed. The residue was then dried and retained for final ignition before use.

The ferruginous and aluminous character of this soil-matrix pointed to the possibility of its acting as a porous body in promoting the formation of nitrogenous compounds, or absorbing and retaining the ammonia supplied to the plants, or that which might be formed from the nitrogenous matter of the seed. In order to ascertain whether any formation of nitrogenous compounds in the manner here supposed occurred, a pot of soil, prepared as for an experiment with a plant, was submitted to the same conditions of air, temperature, moisture, &c., as the pots containing the experimental plants, but no accumulation of combined nitrogen took place.

When volcanic pumice was used, it was powdered until the greater portion was quite fine, and the largest pieces were about the size of peas. The powder was then subjected to long washing in the same manner as the ignited soil, and lastly, dried ready for final ignition before being used.

The necessary mineral constituents were in most cases supplied in the form of the ash of the plant of the description to be grown, or, if this were not practicable, of that of some closely allied kind. In some instances the ash was obtained by burning a quantity of the entire plant when in seed; in others, the seed and the rest of the plant were burnt separately, and a mixture of the two ashes made in the proper proportions. Strongly alkaline ashes (of Leguminous plants) were sometimes saturated with sulphuric acid, and the mixture ignited. The ashes were prepared in large shallow platinum dishes, heated in a current of air in a cast-iron muffle, and the burning was continued until all coaly matter disappeared. Examination failed to detect combined nitrogen in any of the ashes so prepared. A consideration of the chemical constitution of soils suggested a proportion of 0·8 to 1·0 per cent. of ash, and this was the quantity added to the matrices in 1857, but in 1858 only about half as much was employed.

In some cases weak solutions containing phosphoric acid or sulphuric acid were used as well as ash.

The strength of a dilute solution of phosphoric acid was determined by means of a titrated alkali-solution, and it was then neutralised by carbonate of soda. Each pipette measure of the solution given to the plants supplied about 0·01 gramme phosphate of soda. It was only employed in the experiments of 1858.

The sulphuric acid solution, which was also only employed in 1858, was prepared by determining the strength of some very dilute pure acid, in the same manner as that of the phosphoric acid. It was then so far reduced that the pipette measure by which it was applied to the plants contained exactly as much sulphuric acid as the pipette of sulphate of ammonia solution then in use, which corresponded to 0·004 gramme nitrogen.

When ammonia was supplied to the plants, it was given in the form of a weak solution of the sulphate, which was prepared as follows:—Ordinary ammonia-water was distilled from a flask and the vapour condensed in pure distilled water. The strength of the solution was determined by the volumetric method against that of dilute sulphuric acid of known strength, the preparation

of which is described further on. A given volume of the ammonia-liquid was then neutralised by pure dilute sulphuric acid, of which the measure added was determined, and the strength of the sulphate-solution calculated accordingly. It was intended that each cubic centimetre should contain about one-tenth of a milligramme of combined nitrogen, and generally 4 to 6 milligrammes were supplied at once.

The value of each of the above solutions was determined by analysis to insure that its composition was such as was supposed.

The plants were watered with distilled water, in the preparation of which the first two-fifths of the distillate from ordinary water were allowed to escape, and the next two-fifths were collected for further treatment. This water retained traces of ammonia. It was mixed with a little phosphoric acid free from nitric acid, and then re-distilled from a copper vessel, to which a glass condenser was attached.

All parts of the apparatus, the presence of ammonia in which could possibly affect the result, were, after thorough washing both with ordinary and common distilled water, finally rinsed with this pure double-distilled water just before being used.

In the experiments of 1857, common flower-pots were used, and small common white-glazed plates were employed as pans. For the experiments of 1858, observation suggested the kind of pot and pan represented in figs 1, 2, and 3, plate I. The pot was made of the same material as ordinary flower pots, but as light as possible, and it was somewhat less baked. The height and diameter at the top were each five inches, and the diameter at the bottom was four inches. The bottom, and the sides to a distance of one inch from the bottom, were perforated with numerous holes of nearly one-fourth of an inch diameter as shown in figs. 1 and 2. The pan, represented in fig. 3 with the pot placed in it, is made of hard baked and well-glazed stoneware. It is 1·5 inch deep and 5·2 inches in diameter at the bottom. At the top it is curved inwards (A, B, fig. 3), so as to adapt its upper rim to the sides of the pot. These arrangements reduced the surface for evaporation from a given volume of soil, and facilitated the exit of the roots, and the access of air. The pan affords room for an abundance of water, in which the roots develop luxuriantly, and are protected from the direct action of sun-light. Thus, a minimum of evaporation from other sources, and a drier atmosphere, being maintained, evaporation through the plant itself is favoured; and hence

the conditions are provided for a constant supply to the plant of all the mineral and gaseous substances in solution in the fluid of the soil and pan.

In preparation for an experiment, the soil, the ash, and the pot, were simultaneously heated to redness, and the soil and ash, whilst red-hot, were mixed together in the red-hot pot, which was placed upon a red-hot brick, over sulphuric acid, the whole being then covered with a large glass shade, and left to cool. In 1857, from $2\frac{1}{2}$ to 3lbs. of ignited soil were put into each pot; but, in 1858, the lower part of the pot was first filled, to the depth of about one inch, with very coarsely broken up red-hot flint. The greater portion of the ash was mixed with the lower layers of soil, but some was distributed through the whole of it. After cooling sufficiently, the shade was removed, and about 500 cub. centims. of pure distilled water were added to the soil of each pot; and, after ten to twenty hours more, the seeds were put in.

In all the experiments recorded, the plants were grown directly from seeds, sown in soils prepared as above described. A quantity of seed of very good quality being procured, the largest and smallest, or any looking unhealthy, were picked out. Given numbers of the remainder were then weighed, and the average weight per seed was calculated. A few, weighing as nearly as possible the mean weight, were then selected for planting, and a number of others, of equal weight and character, were reserved for the determination of their nitrogen, as a means of estimating the quantity supplied in the seed sown.

The quantity of ammonia in the atmosphere is so small, that, had it been intended to grow the experimental plants in limited volumes without change, the amount of combined nitrogen available to the plants by its means might have been entirely disregarded; but as, for various reasons, it was decided that the plants should grow in an enclosing apparatus through which a current of air passed, it was freed from ammonia, and solids mechanically suspended, by washing in the manner presently to be described, before being admitted into the apparatus.

Owing to the small proportion of carbonic acid in the atmosphere, and to the fact, that a part of it would be absorbed in the washing process just referred to, it was necessary to give a supply of it to the plants artificially. This was obtained by the action of chlorhydric acid upon fragments of marble, and the arrangements for its supply will be described presently, with the rest of the

apparatus. Boussingault found* that the air surrounding a plant might, consistently with healthy growth, contain 8 per cent. of carbonic acid, whilst the normal atmosphere, in which vegetation flourishes, contains only 0·04 per cent. Calculation showed that a minimum of 0·2 per cent of carbonic acid in the air of the enclosing apparatus would supply very much more than was required by the plants: and from the observations of Boussingault it was concluded that 4 per cent. might be adopted as the maximum. Further, our own experiments on the nature of the gas in plants show (as will be seen further on) that the changes in the proportion of carbonic acid in the air of the cells and intercellular passages, and in the fluids of the stem, are much greater and more rapid than those which could take place in the atmosphere of our experimental plants. Moreover, plants derive much of their carbonic acid from aqueous solution absorbed by the roots, and most probably the remainder is taken up by the fluids of the plant before influencing its growth. These absorptions can take place but slowly, so that rapid variations in the proportion of carbonic acid in the atmosphere of the plant, will be accompanied by much less variation within it. It was considered probable, therefore, that there would be no danger in so supplying carbonic acid to the atmosphere of the plants, as to reach the proposed maximum proportion in a short time, and then, by the passage of the air, bring it gradually down to the minimum.

In practice, a little more chlorhydric acid was added at one time to the marble than was necessary to provide 4 per cent. of carbonic acid in the atmosphere of the plants, and the passage of the air was commenced simultaneously. Repeated analyses of the air in the enclosing apparatus showed that the limits of 4 per cent. as the maximum, and 0·2 per cent. as the minimum, were not passed when operating in this way.

The description of apparatus used for each separate experiment in 1858 (and subsequently), to enclose the plants, and to supply them with air, water, carbonic acid, &c., is represented in fig. 1, plate II; and that used in 1857 only differed in some few points, to the chief of which reference will be made.

A, represents a large stoneware Woulfe's bottle, 18 inches in diameter, and 24 inches high. *a* represents the cross section of a leaden pipe $1\frac{1}{2}$ inch diameter (which is connected with a reservoir

* Mémoires de Chimie Agricole et de Physiologie, 1854, p. 441.

of water not shown), and which passes over a series of vessels A, at right angles to the plan of the figure, and is connected with each by the tube *a b*, in which is fixed a stop-cock to open and shut the connexion between the water-supply tube *a* and the vessel A. *c d e* is a leaden exit-tube for air, enlarged at the point *c*, and downwards, until it opens into the vessel A, thus allowing the half-inch safety-tube, *q r s*, to pass through it and down to the bottom of the vessel A, as indicated by the dotted line.

The bottles B and C (which with T, E, and O, are each of about 30 ounces capacity), contain sulphuric acid of sp. gr. 1·85, to a depth of 2½ inches. The tube D D is about 3 feet long and 1 inch diameter, filled with fragments of pumice saturated with sulphuric acid, in which, at *f f* are indentations to prevent the sulphuric acid from draining against the corks. The bottle E contains a saturated solution of ignited carbonate of soda, and its interior is connected with that of the glass shade F, by means of the bent, and caoutchouc-jointed glass tubes *g h*.

The shade F is about 9 inches in diameter and 40 inches in height, but in some experiments, shades 16 inches in diameter and 28 in height were used. *i k* (better indicated in fig. 2, plate II) is the exit tube for the air, and is connected, externally to the shade, with an eight-bulbed apparatus, M, containing sulphuric acid. *u v*, also better indicated in fig. 2, is for the supply of water, or solutions, to the soil; and *n o* is for the escape of condensed water into the bottle O, to the bottom of which passes another glass tube *t*, by means of which the condensed water which collects in it is withdrawn.

w w is a lute-vessel of hard baked and well glazed stoneware, and is, in fact, simply a shallow dish with double concentric sides, the space between which forms a groove for the reception of the shade and of the luting material, which was mercury, and for the passage of the tubes. Fig 4, plate I, is a plan of the stoneware lute-vessel, which shows the groove widened and deepened at four equidistant points for the passage of tubes underneath the shade, and also the hole *n* for the escape of the condensed water. Fig. 5 is a vertical section of the lute-vessel from A to B of fig. 4, through two of the widened and deepened portions of the groove, and through the orifice *n*; and fig. 6 is a vertical section from C to D of fig. 4.

The bottle T contains fragments of marble, from which carbonic acid is evolved by the addition of measured quantities of chlorhydric acid, supplied by means of the tube *y*.

In 1857, blocks of slate 12 inches square and $3\frac{1}{4}$ inches thick, with a circular groove, $\frac{1}{2}$ an inch wide and 2 inches deep, adapted to the diameter of the shades, but widened and deepened for the passage of the tubes, were used instead of the stoneware lutes above described; and the condensed water was withdrawn by means of a bent tube passing from the outside beneath the shade, and extending to the surface of the mercury in the groove within the shade.

On opening the stop-cock below *a*, (fig. II, plate) water flows into the vessel A, from the reservoir with which the tube *a* is in connection. As the pressure increases, the water rises in the safety-tube *q r s*, above the level in A, and air escapes by the tube *c d e*, forces its way through the sulphuric acid in the bottles B and C, through the tube D D, containing pumice saturated with sulphuric acid, then through the solution of carbonate of soda in E, enters the shade F by the tubes *g h*, and passes out through the tube *i k*, and the bulb apparatus M, containing sulphuric acid. Calculation showed that the minimum pressure required to force the air through the apparatus was equal to that of a column of mercury 1·037 inch in height. The difference between the height of the water in A and in the safety tube *q r s*, must be equal to this amount multiplied by the specific gravity of mercury; and the height from the top of the vessel A to *r* being about 12 inches, the whole of the air passed out of A before the water ascended to *r*, and flowed out of *q*; whilst the great height of *d* prevented the water from passing over into the bottle B; an accident which unfortunately happened on a few occasions in 1857, when the air and safety-tubes were somewhat differently arranged.

When the vessel A was full of water, it was let off by a cork hole at the bottom, air being at the same time admitted by the tube *x* at the top.

The minimum pressure upon the inside of the glass shade F would be $\frac{1{\cdot}0 \times 1{\cdot}85}{13{\cdot}6} = 0{\cdot}136$ inch, 1·0 being the difference between the levels of the sulphuric acid in the bulb-apparatus M; but owing to friction, &c., the maximum pressure might be raised to double this calculated minimum.

All the Woulfe's bottles were made as air-tight as possible, by means of very good corks, which, in the cases of E and O, were covered with a cement composed of 8 parts gutta percha, 12

parts common rosin, and 1 part Venice turpentine, well melted together. The glass tube *n o* was also fixed into the lute-vessel at *n* with this cement. At first, tubes of unvulcanised, but afterwards of vulcanised caoutchouc were used for the various joints indicated. The ends of the tubes *t* and *u* were fitted with caoutchouc tubing, into which pieces of solid glass rod were fitted as stoppers.

In 1857, twelve such sets of apparatus, and in 1858 a larger number, were employed. The whole were arranged side by side, on stands of brickwork, in the open air, and were protected from rain, or the too powerful rays of the sun, by a canvas awning which could be drawn over them, or withdrawn, at pleasure. In 1858, two glass cages, such as were used by M. G. Ville, and which he kindly sent over to us, were also employed.

The volume of washed air passed through the apparatus daily, was, in the earlier experiments, that of the vessel A, equal to about two and a-half times that of the shade F, but in the later ones generally twice as much, or more.

The apparatus above described has the following advantages :—

1. When it is once enclosed, and the mercury poured into the groove, the plant is entirely excluded from all external sources of combined nitrogen; and, in case of its being necessary to open the vessel, this can be done with great facility.

2. By means of the tube *n o*, and the bottle O, the water which condenses within the shade is quickly removed from the atmosphere of the plant. The pan in which the pot stands, with its inward-turned rim, allows of a store of water being kept beneath the plant, which, at the same time, is protected from free evaporation. Water is very easily supplied by the tube *u v*, and the bottle O holds as much as can be condensed during several days ; its contents are easily removed by means of the tube *t*, and returned, if required, by the tube *u v*.

3. A simple glass shade is more easily cleaned before commencing the experiment, and is less likely to retain combined nitrogen at its termination, than a complicated metallic framework with panes of glass cemented into it; whilst the presence of oxidisable metallic surfaces is avoided.

4. The only organic matter within the shade is the thin coating of cement by which the tube *n o* is fixed into the hole *n* at the bottom of the lute; and analysis showed, that even if the whole of the cement in contact with the condensed water became decomposed, it

could only yield a fraction of a milligramme of nitrogen, whilst, experiment proved that it did not suffer sensible decomposition when exposed in the open air during a whole year.

5. During the passage of the air, the excess of pressure is upon the inside of the enclosing vessel, instead of, as in the experiments of others, upon the outside, and hence, any leakage would be from within outwards, instead of from without inwards, by which extraneous combined nitrogen might be introduced; and when the air is not passing, any pressure in the opposite direction, due to changes of temperature and barometric condition, can never exceed that required to drive air inwards through the sulphuric acid in the bulb-apparatus M.

6. The part of the apparatus which is most liable to leak, and would be the most damaged by pressure, is subjected to the minimum amount of it, the only pressure exerted upon the glass shade being the amount requisite to force the air through the bulb-apparatus M.

Lastly in reference to the arrangements for experiment, it may be observed, that the proportions of nitrogen and oxygen in the air can be only very immaterially affected by absorption under the influence of the slightly increased pressure in the vessel A; that provided the whole of the carbonic acid of the air were absorbed by the water, this would be of no consequence, arrangements being made for its artificial supply; and, that although the air may take up a considerable amount of water in the vessel A, it must lose most or all of it in passing through the sulphuric acid in the bottles B and C, and over the pumice saturated with sulphuric acid in D D, and the re-dried air will pass too rapidly through the carbonate of soda solution in E for re-saturation, whilst, as the air will be cooler before it enters the shade than within it, it will not be then so near its point of saturation.

The conditions of atmosphere provided were proved to be adapted for healthy growth, by growing wheat, barley, and beans, under the adopted conditions, but in a good garden soil, when luxuriant vegetation was the result. (See fig. 13, plate III.)

The conditions of the artificial soils were shown to be suitable for the purposes of the experiments by the fact, that plants grown in such soils, and in the artificial conditions of atmosphere, developed luxuriantly if only manured with substances supplying combined nitrogen. (See figs. 7–12, plate III).

Taking up the Plants, Preparation for Analysis, Methods of Analysis, &c.

At the termination of growth, the glass shade was washed outside, quicksilver was poured into the groove, to displace from it the condensed water not removable by the arrangement of 1857, or collected in the bottle O of 1858, as the case might be, and the shade was then removed. The previously covered portions of the slate or stone-ware lute were then washed with pure distilled water, and the washings added to the condensed or drain-water. In the experiments of 1858 this fluid was analysed separately, but in those of 1857, it was mixed and dried down with the soil.

The pot with its contents, was removed to a clean table covered with white paper, the plants measured in all their parts, and then cut off at the surface of the soil; the roots were removed, slightly washed from soil and their character noted. The plants were then put into a small wide-mouthed bottle, generally stem and root together, but sometimes they were put into separate bottles. In the experiments of 1857 the contents of the bottles were dried in a water-bath, with a current of air, previously washed with sulphuric acid, passing through the bottle and thence through a solution of a known quantity of pure oxalic acid; but as no appreciable amount of ammonia was thus accumulated, in 1858 a little oxalic acid (in solution) was added to the vegetable matter, and the whole dried in the water-bath without the above precaution.

When dry, the vegetable matter was cut small by means of a pair of clean long scissors reaching to the bottom of the bottle, and it was afterwards still further reduced by grinding up in the mortar when mixed with soda-lime for analysis. When duplicate analyses were made, the matter was carefully divided, so as to ensure equal proportions of stem, fine leafy matter, &c., in each half; so that, if both analyses were successful, the results were mutually confirmatory, or if one portion were lost, the other represented a proportional amount of the whole.

The soil was removed from the pot to a porcelain dish, and a sufficient amount of a solution of oxalic acid added to keep it acid. The mixture was then heated on a sand-bath, stirring constantly, until most of the water was expelled, more fully dried in the water-bath, and then preserved in well-corked bottles for

analysis. The pots were pounded up; those of 1857 being preserved and analysed separately, and those of 1858 mixed with the soil before it was dried with oxalic acid. The pieces of flint at the bottom of the pot were also pounded and mixed with the soil.

For analysis, 150 to 200 grammes of the soil, pot, or mixture, were mixed with about half the volume of soda-lime, the whole put into a large combustion-tube, some soda-lime put in advance of the mixture, and then asbestos, as usual. The combustions were made in charcoal furnaces, and the ammonia collected in titrated sulphuric acid (see p. 141). When very small quantities of nitrogen were evolved, the ammonia from two or three tubes of substance was sometimes collected in the same quantity of acid, so as to diminish the error of titration. It was found, however, to be better to use very small quantities of acid, and to estimate the product of each combustion separately; for, by the former method, if any accident occurred in the second or third combustion, it involved the loss of the determination of the products previously collected.

Preparation of the Titrated Solutions.—A weighed quantity of pure, dry, carbonate of soda was dissolved in water, and water added to a given volume. As a preliminary step, the strength of some dilute sulphuric acid was tested against a given volume of the carbonate of soda solution; and from the data obtained, by further dilution a large quantity of acid was made of about the strength desired. The exact value of this acid was then ascertained. To accomplish this, a given volume of the carbonate of soda solution was put into a beaker, a little litmus added, and the mixture heated over a spirit lamp. The acid was then allowed to flow from a burette until a wine-red colour (indicating the presence of bicarbonate with carbonic acid in solution) was produced. On boiling, the blue colour is restored; acid is added until red; the boiling is repeated until the blue returns; acid again added, and so on, until the solution remains red on the addition of the last drop. The point at which the permanent change takes place in the first trial being known, the experiment is easily repeated so as to ensure great accuracy.

Thus, 50 septems of carbonate of soda solution, of which 1,000 septems contained 6·652 grammes of the salt, required, for neutralization, in six different trials—58·3, 58·2, 58·3, 58·3, 58·2, 58·2; mean 58·25 septems. Hence—

$$\frac{6{\cdot}652}{1000} \times \frac{50}{58{\cdot}25} \times \frac{N}{NaO.CO_2} = \frac{6{\cdot}652}{1000} \times \frac{50}{58{\cdot}25} \times \frac{14}{52{\cdot}98} = 0{\cdot}001508 \text{ gramme N.}$$

The mean of six experiments with a solution of carbonate of soda of another strength gave, in the same way, 0·0015008 gramme nitrogen. The mean, or 0·001504 gramme, was therefore adopted as the amount of nitrogen corresponding to 1 septem of the titrated acid.

As the alkali, to test against this standard acid, a solution of sugar-lime was first employed, but being found liable to constant change, due doubtless to fermentation, a solution of caustic soda was had recourse to. The burette was of small enough diameter to allow of one-tenth of a septem being read off on it, and the alkali-solution was so dilute that it required about 3 septems of it to neutralise 1 septem of the acid. Hence, 1 septem of the alkali-solution corresponded to only about half a milligramme of nitrogen, and the probable error of reading would therefore be only about one-twentieth of a milligramme—an amount much less than would be admissible as error of analysis. In the case of the sugar-lime solution it was found necessary to test its strength against that of the acid every day that it was employed. But the soda-solution, if properly prepared, and well preserved, remained for months unchanged.

Amount and measurement of the Titrated Acid used in Nitrogen Determinations.—It was desirable that at least 3 times as much acid should be used as would be neutralised by the ammonia formed. The acid being more concentrated than the alkali, it required a more exact method of measurement; and pipettes, of which the diameter at the point of reading off was comparatively small, were therefore employed; in the construction of which, care was taken to maintain the same relation of the diameter of the neck at the point of reading to the entire volume in instruments of different sizes—a condition seldom observed by makers of pipettes. When the quantity of nitrogen involved in an analysis was very small (as is the case of the soils and pots in the experiments without nitrogenous manure), only about 6 septems of the titrated acid, measured in a small pipette with a very narrow neck were used, the exact volume of which was of no consequence, it being only essential to ascertain its exact value expressed in septems of the titrated alkali-solution. When the amount of nitrogen involved was larger, as, for example, when

grains were to be analysed, sufficient accuracy was attained when the substance experimented upon contained 5 to 8 milligrammes, or more, of nitrogen.

Combustion-tubes, Bulbs, &c.—The tubes used in the determinations of nitrogen in the soils, pots, &c., were about 3 feet long and about 1 inch in diameter. The bulb-apparatus, was capable of holding two and a-half to three times as much fluid as that usually employed; but the central and lowest bulb, and particularly its tubular connexions with the other bulbs, were very small, so that a small quantity of liquid could close the passage. This arrangement was necessary, owing to the small quantity of acid frequently used, and the large amount of water driven off in the combustion from the large quantities of soil and soda-lime. For the combustion of the experimentally grown plants, smaller tubes were employed; and for the seeds, &c., ordinary combustion-tubing was used.

Soda-lime.—Before use, the soda-lime was ignited with 2 per cent. of pure sugar, in order to ensure its freedom from ammonia yielding matter. It was then slaked with pure distilled water, dried, and kept in well-corked bottles.

Accuracy of the Method for the Determination of Nitrogen by Combustion with Soda-lime, &c.—In order to ascertain the accuracy of the method, some experiments were made upon the determination of small and known quantities of nitrogen, mixed with large quantities of soil previously freed from combined nitrogen as in the preparation of the soils for the plant-experiments. The nitrogenous substance taken was the powdered crystals of purified quadroxalate of ammonia—

$$\left.\begin{matrix}NH_3\\H\end{matrix}\right\}O.(C_2O_3)_4 + 7HO.$$

The results were—

Experiment 1.—50 grammes of prepared soil, mixed with quadroxalate, containing by calculation 0·0024 gramme nitrogen, gave on burning with soda-lime, and determining as above 0·0027 gramme.

Experiment 2.—100 grammes of soil, mixed with quadroxalate, equal by calculation to 0·0035 gramme nitrogen, gave on combustion 0·0037 gramme.

The error of analysis was, therefore, three-tenths of a milligramme of nitrogen with the 50 grammes, and two-tenths with

the 100 grammes of soil. These results were obtained at the commencement of the inquiry, with comparatively large quantities of the titrated acid, and before experience had suggested the precautions to be adopted to reduce the errors of determination to the minimum. They may hence be taken as examples of the maximum errors of analysis, but they are less than would affect the bearing of the results in the investigation on the question of assimilation.

Qualitative Examination for Nitric Acid.—The indigo test, as recently refined by Boussingault,* and the protosulphate-of-iron test, were both employed. When nitric acid was sought for and not found, the negative result was, if practicable, always controlled by the addition to some of the substance under examination of a quantity of nitric acid (in the form of nitrate) less than could affect any conclusions to be drawn from the fact of its presence or absence in the substance in question; and, in all such cases, the re-examination showed the presence of nitric acid.

The method of Boussingault was much more delicate than the protosulphate-of-iron test; but, on the other hand, the latter was much less liable to give deceptive indications, dependent on other circumstances than the presence of nitric acid. In using the protosulphate test, the aqueous extract of the substance under examination (after destroying any organic matter by boiling with permanganate of potassa, &c.), was evaporated to a small volume with excess of fixed alkali, then transferred to a test-tube, and further evaporated till only a few drops remained. A considerable excess of concentrated sulphuric acid was then added, and on the surface of the liquid, a concentrated solution of protosulphate-of-iron was carefully poured, without agitation, by means of a small pipette with a mouth of almost capillary fineness. The characteristic tinge indicated the presence of nitric acid.

Conditions of Experiment requiring Collateral Investigation.

Under this head it is proposed to consider:—1. The possible influence of ozone in promoting the formation of nitrogenous compounds from free nitrogen, either within or in connexion with the

* Ann. Ch. Phys., vol. xlviii (1856), p. 153 et seq.

plant, or within the soil, either directly, or in connexion with the organic matter of the plant. 2. Whether or not there be an evolution of free nitrogen in the decomposition of nitrogenous organic matter. 3. Whether, under the circumstances of the experiments, there would be likely to be a formation of nitrogenous compounds, by the mutual action of nascent hydrogen (evolved by decomposing organic matter) and free nitrogen.

With regard to the first point, ozone may be supposed to occur within the cells and intercellular passages of the plant, either in the gaseous state or in solution, or it may be simply around the plant without existing in its structures. It may be a product of the action of the sun's rays, by virtue of which carbonic acid is decomposed and oxygen evolved, or it may result from other actions to which reference will presently be made.

To ascertain experimentally, if possible, whether ozone were present within the cells or intercellular passages, the gases obtained by exhausting plants placed in water freed from air by boiling, were examined, but no ozone was detected. Other experiments were also made, in which about an ounce respectively of green wheat, barley, oats, beans, and clover, were placed in 500 cub. cent. of carbonic acid water, and the whole subjected to sunlight, but though from 100-200 cub. cent. of gas were obtained, which contained sufficient oxygen to inflame a glowing taper, test-paper placed in it did not indicate a trace of ozone. Granting, however, that ozone may, under certain circumstances, be a product of the decomposition of carbonic acid within the plant, it is still a question whether such conditions would be favourable to its oxidating free nitrogen; an action which will obviously be dependent on the intensity of the reducing power of other substances present. The investigations of Schönbein and others appear to show that, under certain circumstances, nitric acid may be formed by the mutual action of ozone and free nitrogen; but the question is, whether these circumstances are presented in the cells and intercellular passages of growing plants, a point which we have sought to study by the examination of the gases they contain under various circumstances.

Plants, or parts of plants, were put into a flask filled with water which had been freed from air by boiling; a cork, through which a bent glass tube was passed, was then pressed into the flask, filling the tube with the displaced water. The flask was then

placed over a lamp, the water boiled, and the expelled water and gas collected over mercury, the boiling being continued until the vapour produced expelled most of the water collected over the mercury. The gas so obtained, in numerous experiments, consisted entirely of nitrogen and carbonic acid, without any oxygen; from which it is obvious that the reducing power of the carbon compounds in the vegetable cells, was sufficient, under the circumstances, to consume all the oxygen (or ozone) that might be present. But the high temperature at which the experiment was conducted, must have tended very much to increase this action.

In all subsequent experiments a different plan of operation was adopted. The plants were put into a tall glass vessel, 14 inches high, and 1·75 inch in diameter (fig. 7, plate I), the mouth of which was fitted with a long cork, previously well-boiled in bees'-wax, through which two glass tubes, *a* and *b*, are inserted. The vessel being filled with water previously well-boiled and cooled without access of air, the plant is put in and well-shaken to remove adherent air-bubbles. The cork is then forced in, taking care that both the tubes become filled with water, and that no air remain in the vessel. As a further security for tightness, a piece of thick caoutchouc tubing may be drawn over the neck of the vessel, projecting upwards a little above the cork, and the cup thus formed, partly filled with melted wax, forming a layer over the cork and its joints. A funnel is then attached to the tube *b*, by means of a caoutchouc tube which can be closed by a strong pinch-cock. Water being admitted through the funnel into the tube *b*, the tube *a* becomes filled, and it is then brought into connexion, by means of a glass tube and caoutchouc joint fitted with a pinch-cock, with a vessel filled with quicksilver. The connexion being opened, the quicksilver is allowed to flow from the vessel by means of a long tube, of more than barometric length, fitted into the lower part of it, thus forming a Torricellian vacuum in the mercury vessel. The gas from the plant passes over into the vacuum, and by a simple arrangement is collected in an eudiometer tube for examination.

The following table (VIII) shows the amount and composition of the gas obtained in the manner above described, from different plants, *in the shade* :—

TABLE VIII.

Date.	Description.	Total gas collected; cub. cents.	Per cent.			
			Nitrogen.	Oxygen.	Carbonic acid.	Oxygen and carbonic acid.
		Wheat; 1858.				
June 16.	Whole plant.....	57·0	77·72	2·28	20·00	22·28
June 17.	Whole plant.....	55·3	77·94	5·06	17 00	22·06
June 16.	Whole plant.....	57·0	78·60	1·75	19·65	21·40
June 16.	Whole plant.....	55·7	77·38	3·23	19·39	22·62
June 16.	Whole plant.....	65·7	82·50	0·50	17·20	17·50
		Barley; 1857.				
June 24.	Whole plant.....	8·6	85·12	3·93	10·95	14·88
June 24.	Whole plant.....	20·9	81·48	1·97	16·55	18·52
		Beans; 1858.				
June 17.	Whole plants coming into flower	54·3	79 74	5·16	15·10	20·26
June 17.	Whole plants coming into flower	41·5	86·74	4·10	9·16	13·26
June 17.	Whole plants coming into flower	52·5	80·38	4·38	15·24	19·62
June 17.	Whole plants coming into flower	50·4	84·33	4·36	11·31	15·67
		Clover; 1857.				
Aug. 10.	Heads	47·7	85·61	6·00	8·39	14·39
Aug. 10.	Stems and leaves.....	59·8	83·23	2·33	14·44	16·77
Aug. 11.	Heads	91·0	87·15	1·89	10·96	12·85
Aug. 11.	Stems and leaves.....	42·3	78·32	1·31	20·37	21·68

These results show that the reducing power of certain of the carbon compounds of the plant was sufficient to convert nearly the whole of the oxygen (or ozone) present, into carbonic acid, when in the shade.

Over 100 exhaustions were made, precisely as in the case of the last experiments, with the exception that the plants were exposed, during the whole process, to the direct rays of the sun. Table IX exhibits a few of the results obtained:—

TABLE IX.

Date.	How manured, &c.	Total gas collected; cub. cents.	Per cent.			
			Nitrogen.	Oxygen.	Carbonic acid.	Oxygen and carbonic acid.
	Wheat (whole plants); 1858.					
June 22.	Unmanured	44·4	73·65	21·17	5·18	26·35
June 23.	Unmanured	34·8	77·01	21·26	1·73	22·99
June 30.	Unmanured	44·1	72·79	20·86	6·35	27·21
June 22.	Mineral and ammoniacal manure	54·5	73·76	21·29	4·95	26·24
June 23.	Mineral and ammoniacal manure	42·1	78·15	15·44	6·41	21·85
June 25.	Mineral and ammoniacal manure	37·2	78·76	19·09	2·15	21·24
	Grass (whole plants; second crop); 1857.					
Aug. 15.	Mineral and ammoniacal manure	39·0	82·10	16·19	1·71	17·90
Aug. 15.	Mineral and ammoniacal manure	47·8	77·08	15·35	7·57	22·92
Aug. 15.	Mineral and ammoniacal manure	41·6	76·56	21·46	1·98	23·44
Aug. 17.	Mineral and ammoniacal manure	39·9	75·07	23·39	1·54	24·93
Aug. 18.	Mineral and ammoniacal manure	36·8	79·88	15·19	4·93	20·12
Aug. 18.	Mineral and ammoniacal manure	42·3	80·23	15·97	3·80	19·77
	Beans; 1858.					
July 12.	Mineral manure; almost podding	44·3	71·11	18·28	10·61	28·89
July 12.	Farm-yard manure; almost podding	45·8	73·14	10·26	16·60	26·86
July 15.	Unmanured; almost podding	25·9	82·63	15·83	1·54	17·37
July 15.	Mineral and ammoniacal manure; almost podding	30·9	70·55	20·71	8·74	29·45

The general accordance in the proportions of nitrogen throughout this series, together with their general approximation to the amounts observed in the preceding series, and the consequent similarity in the range of the sums of the two remaining gases—

carbonic acid and oxygen—point to the character of the change by virtue of which the proportion of carbonic acid is diminished, and that of oxygen increased. The variations are, nevertheless, somewhat considerable; nor do we feel confidence in referring them to any other than accidental causes. There can be no doubt, however, that the carbonic acid shown to exist in the plants in the shade yields the oxygen evolved in the sunlight.

The results which follow will show the influence of the time of action of the sunlight on the plant, upon the relative proportions of carbonic acid and oxygen.

Duplicate quantities of plant were operated upon, both being prepared in the shade; the vessels were then excluded from the light by means of a thick paper covering; and, in this condition, each was attached to a Torricellian exhauster (the apparatus above described). The covering being then removed from one of the vessels, exposing it and its contents to the direct rays of the sun, and the other remaining covered, the exhaustion of both was then commenced immediately, and the action continued for half-an-hour. The following results were obtained in this manner:—

TABLE X.

Date.	Description of plant.	Conditions during exhaustion.	Total gas collected.	Per Cent.			
				Nitrogen.	Oxygen.	Carbonic acid.	Oxygen and carbonic acid.
(1858)			cub. cents.				
	Beans.	In dark ..	25·7	66·93	2·33	30·74	33·07
		In sunlight	36·4	69·78	8·24	21·98	30·22
July 22.	Oats.	In dark ..	28·3	81·63	3·53	14·84	18·37
		In sunlight	25·9	70·27	13·13	16·60	29·73
July 23.	Oats.	In dark ..	26·4	73·11	8·33	18·56	26·89
		In sunlight	22·7	72·25	16·74	11·01	27·75
July 28.	Oats.	In dark ..	27·4	68·25	5·11	26·64	31·75
		In sunlight	29·2	67·47	19·86	12·67	32·53
July 23.	Oats.	In dark ..	31·4	77·39	6·69	15·92	22·61
		In sunlight	21·7	76·50	16·59	6·91	23·50

The results clearly indicate the ready transformation, in sunlight, of carbonic acid into a solid carbon-compound and free oxygen; and they have an important bearing on the question under con-

sideration, showing, as they do, the powerful reducing action exerted upon the carbonic acid under the influence of the sun's rays.

The experiments next cited were arranged to show whether the reduction of the carbonic acid was more probably due to the action of the sunlight at the moment of the passage of the gas through the walls of the cell, or whether the oxygen were liberated within the growing cell. Duplicate portions of plant were prepared exactly as in the experiments last referred to, and both were kept in the dark for some time before commencing the exhaustion; then, one being still covered, and the other exposed to sunlight, both were submitted to exhaustion for four or five minutes only, increased quantity of plant being operated upon in order to obtain sufficient gas during this short period. Table XI gives the results so obtained :—

TABLE XI.

Date.	Description of plants.	Conditions during exhaustion.	Total gas collected.	Per Cent.			
				Nitrogen.	Oxygen.	Carbonic acid.	Oxygen and carbonic acid.
(1858)			cub. cents.				
July 30.	Oats.	In dark ..	41·7	72·42	3·6	23·98	27·58
		In sunlight	42·5	72·23	4·71	23·06	27·77
July 30.	Oats.	In dark ..	55·7	71·46	3·23	25·31	28·54
		In sunlight	43·3	69·98	3·23	26·79	30·02
July 30.	Oats.	In dark ..	37·9	83·11	6·86	10·03	16·89
		In sunlight	38·5	77·14	9·09	13·77	22·86
July 31.	Oats.	In dark ..	34·4	78·49	7·27	14·24	21·51
		In sunlight	41·8	75·84	7·89	16 27	24·16

It would appear that carbonic acid can pass through the cell-wall under the influence of sunlight without suffering decomposition, and hence that the oxygen yielded by a plant which has been for some time exposed to the direct rays of the sun, existed as such in the cell before the exhaustion. The slight preponderance of oxygen in the gas exhausted in sunlight was doubtless due to its action upon the carbonic acid within the cell during the short period of the operation, just as when the plant is subjected to ordinary atmospheric pressure.

In order to bring out more clearly the influence of sunlight before the exhaustion, experiments were made in which duplicate quantities of plant were each covered for some time, the paper was then removed from one, and then, after an interval of from 20 to 30 minutes, the exhaustion of both was commenced, and continued for 10, 15, or 20 minutes. The following results were obtained:—

TABLE XII.

Date.	Description of plant.	Conditions before and during exhaustion.	Total gas collected.	Per cent.			
				Nitrogen.	Oxygen.	Carbonic acid.	Oxygen and carbonic acid.
			cub. cents.				
July 31 ..	Oats.	In dark ..	24·0	77·08	3·75	19·17	22·92
		In sunlight	34·5	68·69	24·93	6·38	31·31
August 2.	Oats.	In dark ..	18·6	68·28	10·21	21·51	31·72
		In sunlight	39·2	67·86	25·25	6·89	32·14
August 2.	Oats.	In dark ..	30·7	76·87	8·14	14·99	23·13
		In sunlight	26·5	69·43	27·17	3·40	30·57
August 2.	Oats.	In dark ..	17·0	79·41	7·65	12·94	20·59
		In sunlight	28·6	76·22	18·53	5·25	23·78
August 3.	Oats.	In dark ..	29·8	81·88	6·38	11·74	18·12
		In sunlight	32·1	66·36	30·53	3·11	33·64
August 3.	Oats.	In dark ..	11·6	65·52	6·90	27·58	34·48
		In sunlight	23·1	70·56	20·35	9·09	29·44
August 3.	Oats.	In dark ..	17·0	80·00	5·88	14·12	20·00
		In sunlight	19·7	73·10	22·33	4·57	26·90

The comparison of these results with those in Table XI, together with a consideration of the fact that, as soon as the pressure was removed, the gas was evolved from all parts of the leaf, and not from the surrounding water, shows that the oxygen must have been liberated and retained within the cells until the instant of exhaustion.

The results of this part of the enquiry may be briefly summed up as follow:—

1. Carbonic acid, within growing vegetable cells and intercellular passages, suffers decomposition very rapidly on the penetration of the sun's rays, oxygen being liberated, and remaining within the plant, or being evolved from it.

2. Living vegetable cells, in the dark, or not penetrated by the direct rays of the sun, consume oxygen very rapidly, carbonic acid being formed.

3. Hence, the proportion of oxygen must vary greatly, according to the position of the cell, and to the external conditions of light; and it will oscillate under the influence of the reducing force of carbon-matter (forming carbonic acid) on the one hand, and that of the sun's rays (liberating oxygen and forming carbon-compounds containing less oxygen than carbonic acid) on the other. Both actions may go on simultaneously, according to the depth of the cell; and, according to the laws in conformity with which the diffusion of gases, and their passage through tissues, take place, the oxygen of the outer cells would be continually penetrating to the deeper cells, and there oxidising carbon-matter, whilst carbonic acid would pass in the opposite direction, and be decomposed under the influence of sunlight in the outer cells; and the once outer cells, as they become more deeply buried, may gradually pass from the state in which the sunlight is the more powerful, to that in which the carbon-matter is the more powerful reducing agent—from the state in which there is a flow of carbonic acid to them, and of oxygen from them, to that in which the reverse action takes place. Thus, oxidised products—acids, saccharine matter, &c.—may be formed in the deeper cells, and in the outer cells more highly carbonised substances, which, in their turn, become oxidised when buried deeper.

4. The great reducing power operating in those parts of the plant where ozone is most likely, if at all, to be evolved, seems unfavourable to the oxidation of nitrogen; that is, under circumstances in which carbon-matter is not oxidised, but, on the contrary, carbonic acid is reduced, and, when beyond the influence of the direct rays of the sun, the cells seem to supply an abundance of the more easily oxidised carbon-matter, should free oxygen, or ozone, be present. Further, on the assumption that nitrates are available as a source of nitrogen to plants,* if it were admitted that nitrogen was oxidated within the plant, it must be supposed (as in the case of carbon) that there are conditions under which an oxygen-compound of nitrogen may be reduced

* In reference to this point, it may be mentioned that several specimens of green wheat and grass, which had been liberally manured with nitrate of soda, were examined for nitric acid, but no trace of it was found in them.

within the organism, and that there are others in which the reverse action, namely, the oxidation of nitrogen, can take place.

5. Bearing upon the questions under consideration, but illustrated by experiments to be referred to further on, it may be stated, that so great is the reducing power of certain carbon-compounds of vegetable matter, that when the growing process has ceased, and all the free oxygen in the cells has been consumed, water is decomposed, and hydrogen evolved; but, as the action does not continue long, it would appear either that the cell-matter loses its reducing power after being slightly oxidized, or, more probably, that the cell provides a certain amount of matter more easily oxidized than the remainder.

The suggestion arises, whether ozone may not be formed under the influence of the powerful reducing action of the carbon-compounds of the cell on the oxygen eliminated from carbonic acid in sunlight, rather than under the direct action of the sunlight itself—that is, in a manner analogous to that in which it is ordinarily obtained by allowing oxygen to come into incomplete or only instantaneous contact with phosphorus? Certain carbon-compounds of the vegetable cell have a great affinity for oxygen in the dark, and the oscillations of the affinities (due to the degree of light and to the depth of the cell) would afford conditions somewhat similar to those under which ozone is produced in the presence of phosphorus. But, even were the action as here supposed, it may be questioned whether the ozone would not be at once destroyed in contact with the carbon-matter present. It is more probable, however, that the ozone said to be observed in the vicinity of vegetation, is due to the intense action of the oxygen of the air upon minute quantities of volatile hydro-carbons emitted by the plants, than to any action within the cells; and it is in favour of this view, that ozone has been observed most readily in the vicinity of such plants as emit freely essential oils.

If ozone be found in any way in connexion with the growing plant, it might be supposed to act in an indirect, if not in a direct manner, as a source of combined nitrogen in experiments on the question of the assimilation of free nitrogen by plants—(1) by oxidating the nitrogen dissolved in the water within the apparatus, (2) by forming nitrates in contact with the moist, porous, and alkaline soil, (3) by oxidating the free nitrogen in the cells of the older roots or that evolved in their decomposition.

With a view to the points above suggested, experiments were made to ascertain the influence of ozonous air upon organic matter, and on certain porous and alkaline bodies, under various circumstances. For the generation of the ozonous atmosphere, three glass carboys, each of about 40 litres capacity, were fitted with stoneware stoppers, through which glass tubes passed, connecting the three together, the joints being made with calcined gypsum cement. The bottom of each vessel was covered with water to the depth of from a quarter to half an inch, so that, on pieces of phosphorus being dropped in, they were partly covered by the fluid. Another tube, which could be opened or closed at pleasure, was fixed through each stopper for the supply of water and fresh phosphorus, as needed. A gasometer, of 2 cub. feet capacity, was connected by a glass tube with the first of the three vessels, by which means air could be forced through them in a continuous stream. The air, on passing out, was led first through a wash-bottle, and then into a glass vessel, from which, by means of eleven glass tubes passing from it, it was distributed into as many bottles, containing, respectively, the substances to be submitted to the action of the ozone, each bottle being fitted with an exit tube, in which were fragments of pumice, saturated with sulphuric acid. The following were the substances or mixtures operated upon:—

(1) ¾lb. of ignited soil, moistened with 100 cub. centims. water; this being just sufficient, to make it slightly coherent.

(2) ¾lb. of ignited soil, 300 cub. centims. water, 2·5 ounces boiled starch, and 2·5 ounces dry starch.

(3) ¾lb. of ignited soil, 200 cub. centims. water, and 2·5 ounces sawdust.

(4) 2·5 ounces sawdust, and 100 cub. centims. water.

(5) ¾lb. of ignited soil, 200 cub. centims. water, and 2·5 ounces bean-meal.

(6) ¾lb. of ignited soil, 150 cub. centims. water, and 2·5 ounces bean-meal.

(7) 2·5 ounces bean-meal, and 50 cub. centims. water.

(8) 1lb. garden soil.

(9) ¾lb. of slaked lime, and 2·5 ounces bean-meal, made slightly pasty with water.

(10) ¾lb of slaked lime, some starch, and sawdust, made slightly pasty with water.

(11) 2·5 ounces of boiled starch, 2·5 ounces fresh starch, and 200 cub. centims. water.

All the bottles stood before a window where the sun shone directly upon them most of the day, as it did also for some hours on the balloons. The experiment commenced in April, and continued through the summer and part of the autumn, and the thermometer in the room frequently stood at 25° to 29° C. About 9 o'clock every morning, and once or twice more during the day, the cylinder of the gasometer was raised, and by its gradual depression a slow current of air was passed through the apparatus during about two hours. The amount of ozone passed was so great, that vulcanised caoutchouc tubing, first used for the joint with the tube of the wash-bottle, was cut off by the passage of a few gasometerfuls of air; and the joint was then made by means of a piece of larger glass tubing passed over the point of contact of the tubes to be connected, and closed at the ends with rings of cork well fitted upon the smaller tubes. Every three or four days a small piece of phosphorus was dropped into each balloon.

Until the beginning of July the wash-bottle was filled with large lumps of pumice, and about half full of a solution of caustic potass, which, by the rapid bubbling of the ozonous air through it, kept the pumice moist. An examination of this liquid, with the washings of the pumice, failed to show any trace of nitric acid. From the beginning of July, the alkaline wash was replaced by pure water, and, at the termination of the experiment, these washings also gave no indication of nitric acid.

At the termination of the experiment, a portion of each substance or mixture was exhausted with water, and the extract concentrated by boiling, after the addition of permanganate of potassa to destroy the organic matter. The excess of permanganic acid was removed by carbonate of lead, and the clear solution filtered off and tested for nitric acid; but in no case, excepting that of the garden soil (which examination showed to contain it before being subjected to the action) was there any indication of its presence.

It is not, indeed, hence inferred, that under no circumstances can nitric acid be formed by the action of ozone, on nitrogenous compounds of the ammonia class, or the nascent nitrogen evolved from them, or even in connexion with non-nitrogenous bodies, or porous substances permeated with gaseous nitrogen, or in the atmosphere itself; or that the nitric acid in soils is not in part due to some of these actions. But, considering the negative result with large quantities of ozonous air, acting upon

organic matter, soil, &c., in a wide range of circumstances, and for so long a period, it is believed that no error in the results of the experiments on the assimilation of free nitrogen by plants will arise from the action of ozone upon free nitrogen, providing to the plants an unaccounted supply of combined nitrogen.

It may be here observed that, if from the recent results of Schönbein, on the formation of nitrogen-compounds under the influence of evaporation, we are to conclude that the evaporation of water by plants during growth is a constant source of such formation, it would be difficult to arrange an experiment on the question of the assimilation of free nitrogen by plants that would not be open to objection; for there must then be always a gain of combined nitrogen in the experiment due to the action supposed. Or, if such formation be the constant result of evaporation from the surface of the globe (whether land or water), the products can hardly be supposed to become in any material degree distributed through the atmosphere: for, independently of the character and condition of the products, the amount of combined nitrogen brought down from it by aqueous deposition in various forms is too small in proportion to that annually available for the vegetation of a given area, to give countenance to such a supposition.

Numerous experiments were made to determine whether free nitrogen was evolved during the decomposition of nitrogenous organic compounds. Two obvious methods of investigation presented themselves:—1, to allow the decomposition to take place under circumstances in which any free nitrogen evolved might be collected and estimated; 2, to collect and estimate the compounds of nitrogen formed, and reckon the loss of nitrogen as free nitrogen evolved.

Reiset, operating according to the first of these methods, submitted nitrogenous animal and vegetable substances to decomposition under an inclosing vessel, into which he passed oxygen as that of the air was consumed, and the result was an increase in the amount of nitrogen. Operating according to the second method, M. G. Ville concluded that, in several cases, about one-third of the nitrogen of the substance submitted to decomposition was evolved in the free state. Again, as already shown, M. Boussingault found a loss of nitrogen in his experiments on the assimilation of free nitrogen by plants when he used nitrogenous organic matter as manure.

In our own experiments, a given weight of nitrogenous organic matter, the percentage of nitrogen in which was determined, was mixed with burnt, washed, and re-ignited soil, or pumice, and put into a bottle of about 360 cub. cents. capacity (see B, plate I, fig. 8), and a proper quantity of water added. The bottle was closed with a cork, through which two bent glass tubes passed, externally in opposite directions, one connected with an eight-bulbed apparatus, A, containing sulphuric acid, and the other with a similar apparatus, C, containing a solution of oxalic acid, from which passed a bent tube, extending, through a cork, to the bottom of a second bottle, D, containing sulphuric acid; and through the cork of the bottle D another tube, E, also passed, but did not dip into the acid. On drawing air at E, a current was established inwards through the sulphuric acid in A, by which it was washed free from ammonia, through the bottle B with the decomposing organic matter, through the oxalic acid in C, by which the absorbable gaseous products were retained, and so on. At the termination of the experiment, the combined nitrogen remaining in B, and that absorbed by the oxalic acid in C, being determined, the amount of nitrogen given off in the free state was estimated by difference.

In 1857, six experiments were made, two with wheat-meal, two with barley-meal, and two with bean-meal, known quantities of each being mixed, respectively, with about 100 grammes of prepared soil, or about 60 grammes of prepared pumice, the mixtures filling the bottles B to the depth of about two inches, and sufficient water being added to bring the mass into an agglutinated condition. The six sets of apparatus were placed before a large window, where, during the middle of the day, the sun shone directly upon them. Several litres of air were drawn, by the mouth, through each apparatus daily; and the experiment was continued from June 10 to October 8. After a day or two, the gas had a more or less disagreeable taste, and the odour of decomposing organic matter. The following statement condensed from the notes taken, shows the condition of the several mixtures at the termination of the experiment:—

1. Wheat-meal and pumice.—Slightly mouldy; odour of decomposing organic matter; quite moist, particles of pumice adhering together.

2. Wheat-meal and soil.—Slightly mouldy on the surface;

odour as No. 1; the mass moist, but not sufficiently so for the particles of soil to agglutinate.

3. Barley-meal and pumice.—Not mouldy; odour like Nos. 1 and 2, but more intense, and sour, like fermenting malt; the mass wet and clammy.

4. Barley-meal and soil.—Not mouldy; odour like No. 3; sufficiently moist to agglutinate.

5. Bean-meal and pumice.—A little mould on the surface; odour very disagreeable and putrescent; the mass wet and clammy.

6. Bean-meal and soil.—Very similar to No. 5, but rather more wet and pasty.

In every case, carbonic acid was evolved on the addition of oxalic acid to the mass, preparatory to evaporating to dryness; and the most from the bean-meal with soil. A known proportion, about one-half of each dried mass, was burnt with soda-lime; and the remainder reserved for the determination of nitrates, if present. However, the aqueous extract of the mass in no case indicated nitric acid; though, on then adding 0·001 gramme of nitric acid to the residual mass, and re-extracting with water, its presence was always indicated. The following Table gives the numerical results of the six experiments:—

TABLE XIII.

	Substances submitted to experiment.				Nitrogen after decomposition.		
	Description of organic matter.	Description of matrix.	Quantity of meal taken.	Quantity of nitrogen.	Total by soda-lime.	Not recovered.	
						Actual quantity.	Per cent.
			grms.	grms.	grms.	grms.	
1.	Wheat-meal.	Ignited pumice	2·0585	0·0370	0·0338	0·0032	8·51
2.	Wheat-meal.	Ignited soil ..	2·1282	0·0383	0·0335	0·0048	12·53
3.	Barley-meal.	Ignited pumice	2·2495	0·0380	0·0368	0·0012	3·16
4.	Barley-meal.	Ignited soil ..	2·0980	0·0355	0·0309	0·0046	12·96
5.	Bean-meal ..	Ignited pumice	2·0650	0·0803	0·0741	0·0062	7·72
6.	Bean-meal ..	Ignited soil ..	2·0800	0·0809	0·0823	(+0·0014)	+(1·73)

With one exception (in which the gain of nitrogen is within the range of error of analysis), all the experiments show that a part of

the nitrogen of the decomposing organic matter passed into a state in which it could not be estimated by the soda-lime process. Neither did it exist as nitric acid. It would appear, therefore, that there was an evolution of free nitrogen. But, although so large a proportion of the total nitrogen passed off in some form, yet scarcely a trace of ammonia was given off from the mass; for, on distilling the oxalic acid in C with an excess of caustic potassa, in only one case (that of the bean-meal and pumice) was any ammonia indicated, and then it was equal to only 0·002 gramme nitrogen.

The experiments, the results of which are yet to be recorded, were arranged with some reference to the question of the character and extent of the decomposition, and of the part played by water in the process.

In 1858, a set of nine experiments was made, embracing a wide range of conditions as to moisture, in some of which were included the circumstances of germination, early growth, and subsequent decay of the products, and in which the intermediate stages and final extent of decomposition were more closely considered, the former by periodical inspection, and observation on the character of the odour, and the latter by a further examination of the remaining products. Although soil and pumice indicated no special difference of result, both were still used; about 175 to 200 grammes of the former, or 120 to 150 grammes of the latter being employed. Reference to Tables XIV and XV will sufficiently show the other conditions of the several experiments. The description of apparatus was the same as that used in 1857 (fig. 8).

The mixtures: with 50 cub. cent. of water added were in the condition of a rather moist soil; those with 40 cub. cent. were much drier, having no tendency to agglutination; and those with 100 cub. cent. were very wet, having some free water above the solid matters. The seeds sown with 50 cub. cent. germinated in a few days, and the bottles, B, were soon filled with vegetable matter (the beans especially developing a very large amount of root, as well as stemmy and leafy matter); but those with 100 cub. cent. water did not germinate, but in a few days showed decomposition. The mixtures of meal and soil also soon showed signs of decomposition, though the odour from them was less foul than from the whole seed and 100 cub. cent. water, which, throughout, were the most disagreeable; and it may be observed that the water at first resting above the solid matters disappeared so rapidly, with active decomposition, as to lead to the conclusion

that some of it was consumed in the process. There was in no case any ozone re-action to test paper. With these few general remarks, we may omit here a record of the detailed observations periodically made on the progress of the decomposition; adding only, that on July 1st (the experiments having commenced in January) 100 cub. cent. of water were added to each, and on August 28th, when the experiment was terminated, there still remained, in all the cases, a layer of from $\frac{1}{4}$ to $\frac{1}{2}$ an inch of fluid over the solid matter, the condition of which was as follows:—

Wheat (*a*)—Seeds, in soil, with 50 cub. cent. water: very little odour, and not unpleasant; supernatant fluid colourless; the organic matter thoroughly decomposed, only slight remains of stems and leaves being visible. The addition of oxalic acid to the mass preparatory to evaporation to dryness, caused a copious evolution of carbonic acid.

A similar evolution of carbonic acid took place in every one of the experiments.

Wheat (*b*)—Seeds, in pumice, with 100 cub. cent. water: supernatant fluid colourless; a disgusting mouldy odour, the form of the grain retained, but the contents disappeared, and the husks filled with fluid.

Wheat (*c*)—Meal, in soil, with 40 cub. cent. water: supernatant fluid of a yellowish colour and muddy; the mass emitted a foul, disagreeable odour, though less intense than that of the corresponding barley.

Barley (*a*)—Seeds, in soil, with 50 cub. cent. water: the organic matter thoroughly decomposed; stems, roots, and leaves no longer distinguishable; other conditions much as wheat (*a*).

Barley (*b*)—Seeds, in pumice, with 100 cub. cent. water: supernatant fluid clear; the pumice covered with a black coating of organic matter; the odour of the air above the mixture exceedingly disgusting, resembling that of decaying human excrements; traces of sulphide of hydrogen perceptible; the form of the seeds preserved, but the husks contained only fluid.

Barley (*c*)—Meal, in soil, with 40 cub. cent. water: supernatant water yellowish; odour musty, but not very disagreeable; very slight traces of organic matter perceptible.

Bean (*a*)—Seeds, in soil, with 50 cub. cent. water: the organic matter well decomposed; odour musty.

Bean (*b*)—Seeds, in pumice, with 50 cub. cent. water: only

very indefinite skeletons of stems, leaves, and roots remaining; odour musty, but not diagreeable.

Bean (*c*)—Meal, in soil, with 40 cub. cent. water; supernatant fluid slightly yellow; odour musty, but not offensive.

After drying with oxalic acid, any slight remains of organic matter had become brittle; and in every case, excepting where 100 cub. cent. of water had been originally added (when the husks remained visible), the mass had the appearance of clean soil, or pumice, without organic matter.

In a few instances, the sulphuric acid in D became slightly brown, indicating the passage into it, through the oxalic acid, of some more complex carbon-compound than carbonic acid; and we have observed phenomena of a similar kind in some other cases.

The following Tables, XIV and XV, show the conditions of the several experiments, and the numerical results obtained, the former relating more particularly to the amount and proportion of the original *carbon*, and the latter to those of the original *nitrogen*, remaining after the decomposition, or given off during the process :—

TABLE XIV.

Substances involved in the experiment.				Weight of organic matter.		Carbon.			
Organic matter.		Matrix.	Water added.	Fresh.	Dry.	Before decomposition.	After decomposition.	Loss in decomposition.	
Description.	Condition.							Actual quantity.	Per cent.
			cub. cent.	grms.	grms.	grms.	grms.	grms.	
1. Wheat	a. 171 seeds	Ignited soil	50	8·0475	6·7438	3·1089	0·9274	2·1815	70·17
	b. 171 seeds	Ignited pumice	100	8·0715	6·7639	3·1182	0·9178	2·2004	70·56
	c. Meal.....	Ignited soil	40	9·8810	8·2803	3·8172	1·3199	2·4973	65·42
2. Barley	a. 163 seeds	Ignited soil	50	8·0440	6·7127	3·0523	0 9598	2·0925	68·55
	b. 163 seeds	Ignited pumice	100	8·1360	6·7895	3·0872	1·1952	1·8920	61·28
	c. Meal.....	Ignited soil	40	8·9671	7·4830	3·4025	1·0995	2·3030	67·68
3. Beans	a. 7 seeds...	Ignited soil	50	5·7830	4·5830	2·2915	0 8511	1·4404	62·86
	b. 7 seeds...	Ignited pumice	50	6·4700	5·1275	2·5637			
	c. Meal.....	Ignited soil	40	6·1750	4·8937	2·4468	0·9778	1.4690	60·04

TABLE XV.

Substances involved in the experiment.				Total nitrogen.				Nitrogen obtained as ammonia by distillation with weak alkali.			
Organic matter.		Matrix.	Water added.	Before decom. position.	After decom-position.	Loss (or gain).		From oxalic acid in C.		From total products.	
Description.	Condition.					Actual quantity.	Per cent.	Actual quantity.	Per cent.	Actual quantity.	Per cent.
			cub. cent.	grms.	grms.	grms.		grms.		grms.	
1. Wheat	a. 171 seeds	Ignited soil	50	0·1392	0·1398	+0·0006	+0·43	0·00038	0·273	0·0429	30·83
	b. 171 seeds	Ignited pumice	100	0·1396	0·1214	0·0182	13·08	0·00002	0·014	0·0573	41·06
	c. Meal.....	Ignited soil	40	0·1709	0·1680	0·0029	1·74	0·00040	0·234	0·0197	11·49
2. Barley	a. 163 seeds	Ignited soil	50	0·1247	0·0746	0·0501	40·20	0·00055	0·441	0·0157	12·64
	b. 163 seeds	Ignited pumice	100	0·1261	0·1052	0·0209	16·62	0·00002	0·016	0·0294	23·39
	c. Meal.....	Ignited soil	40	0·1390	0·1311	0·0079	5·66	0·00039	0·280	0·0166	11·97
3. Beans	a. 7 seeds...	Ignited soil	50	0·2417	0·2107	0·0310	12·84	0·00341	1·424	0·0140	57·91
	b. 7 seeds...	Ignited pumice	50	0·2704	0·2380	0·0324	11·99	0·00242	0·895		
	c. Meal.....	Ignited soil	40	0·2581	0·2267	0·0314	12·16	0·00060	0·232	0·1039	40·25

The results in Tables XIII and XV are mutually confirmatory in their more general indications; and they agree in showing no tangible relation between the nitrogen-products and the varied circumstances of decomposition. In some cases there has been no, and in others very great evolution of free nitrogen—so great, indeed, that we made repeated analyses to satisfy ourselves of the truth of the result.

The physical condition of the several substances at the termination of the experiment, as also the comparative uniformity in the proportion of carbon given off (see Table XIV), might lead to the conclusion that the decomposition had proceeded about equally far in all cases; but whilst the proportion of carbon given off ranged between 60 and 70 per cent. of its original amount, that of the nitrogen varied coincidently from 0 to 40 per cent. of the original amount. Again, the proportion of the nitrogen which was retained in the mass, or absorbed in the oxalic acid in C, in such form as to be given off as ammonia on distillation after being rendered weakly alkaline, and which probably existed, therefore, in the products as ammonia, ranged from 12 to 58 per cent. of the total quantity involved in the experiment; whilst the proportion evolved from the mass during the decomposition and retained in the oxalic acid solution (C), varied from 0 to about 1·5 per cent. of the original amount. There would seem, in fact, to be no relation between the loss of carbon, the loss of nitrogen, the formation of ammonia, and the evolution of it from the mass during decomposition, on the one hand, and the circumstances of

matrix, moisture, growth, decay, &c., on the other, which can with safety be considered as exhibiting cause and consequence.

It may, however, be concluded, that under particular, and apparently rare circumstances of the decomposition of nitrogenous organic matter, there is no loss of nitrogen evolved in the free state, but that, under a wide range of circumstances, a considerable loss of nitrogen takes place; and whilst the proportion of the nitrogen taking such form that it may be driven off as ammonia on the distillation of the products with a weak alkali-solution, varied from one-eighth to more than one-half of the total, the amount evolved from the mass as ammonia during decomposition was quite inconsiderable.

Independently of the importance of these facts, considered in connection with the conditions which may be involved in an experiment on the question of the assimilation of free nitrogen by plants, it is obvious that they have a very important bearing on the practical question of the management of the manure-heap, and as such, require further investigation to ascertain the causes of the differences of result manifested, in order, if possible to control them. The results also point to the probable insignificance of the loss of nitrogen from decomposing manure in the form of ammonia, a supposed evil to which the attention of agricultural chemists has been especially directed, whilst the apparently much larger loss, as free nitrogen, has not at all been considered.

The question arises, what is the character of the action by which nitrogenous compounds are decomposed with the evolution of free nitrogen? It may be—(1) of an oxidizing character analogous to that of chlorine on ammonia; (2) of a reducing character similar to that of many substances upon the oxygen compounds of nitrogen; (3) these two actions may operate in succession the one to the other.

The nitrogen in the organic substances submitted to decomposition, doubtless existed in a condition more analogous to a hydrogen, than to an oxygen-compound of it; and the researches of Hofmann would lead us to suppose that the nitrogen-compounds in question were of the ammonia class. They are more difficult to oxidize into nitric acid than is ammonia, but their transition into ammonia is extremely easy; and, since ammonias yield free nitrogen under the influence of oxidising forces, it may be inferred that it has been under the influence of such forces that the nitrogen has been set free in the experiments recorded. Pelouze

has remarked* that nitrates are converted into ammonia in contact with decomposing organic matter; and experiments of our own have shown that, during the decomposition of organic matters in contact with nitrates, free nitrogen is not evolved.

The experiments next referred to bear upon these points.

After several qualitative experiments, on a smaller scale, about half a pound of a mixture of wheat, barley, and beans, was put into the long narrow glass vessel of about 500 cub. cents. capacity (plate I, fig. 7), which was then filled with well-boiled water, and closed with a cork, through which two glass tubes (*a* and *b*) passed, the ends of which were fitted with caoutchouc tubing, for closing with pinchcocks, or connexion with the Torricellian exhauster. The vessel having been so connected with the exhauster for several hours, to remove the gaseous nitrogen from the seeds, it was then inverted in mercury, the tube *b* opened under that fluid, and the whole placed in sunlight to favour decomposition. This was done on August 28 (1858); the seed soon swelled, and on August 30 well-marked decomposition had set in. On September 13, the vessel was about two-thirds full of gas, and so much water was displaced, that part of the seed was above the remaining water, in the gas, which commenced bubbling out through the tube *b*. The arrangement so remained until October 5, when 400 cub. cents. of gas were collected, of which the percentage composition was as follows:—

	Carbonic Acid.	Hydrogen.	Nitrogen.
Experiment 1....	64·87	34·83	0·30
Experiment 2....	64·54	35·46	traces

The quantity of gas evolved points to the extent of the decomposition; the amount of carbonic acid and hydrogen shows how great must have been the reducing force exerted; and the small quantity of nitrogen, which was probably due to accident, indicates that free nitrogen was not a product of the action.

The vessel was again filled with boiled water, again connected for some time with the Torricellian exhauster, and again placed in its former position in the sunlight. On November 17, only a few bubbles of gas having been evolved, the vessel was removed into a room, the temperature of which varied from a few degrees above the freezing point to about 24° C. On December 12, the gas

* Comptes Rendus, xliv, p. 118.

collected without exhaustion measured only 6·1 cub. cents., of which 4·6 were absorbed by potassa, and the remainder was combustible and contained no appreciable amount of free nitrogen.

Five grammes of nitrate of potassa were now put into the vessel (with the same organic matter), and it was replaced in the room as before. On May 25, 1859, the vessel having been heated up to 30° C. several times during the interval, only 4 cub. cent. of gas were collected, one-fourth of which was carbonic acid, and the remainder combustible.

The vessel was now placed in sunlight again, but up to the middle of June no more gas was evolved. The fluid still contained nitrate. The vessel was now half-filled with oxygen; but after ten days not one-fourth of the supplied oxygen had been consumed.

The total gas being removed, oxygen was conducted into the vessel until the greater part of the fluid was driven out, leaving the partly decomposed seeds in an atmosphere of this gas. The apparatus so arranged was placed in the sunlight, and remained there during some very warm weather, when, on July 12, the gas collected contained in 100 parts—carbonic acid 20, oxygen 79, nitrogen 1; but as, by accident, a little air had been admitted into the vessel, the small quantity of nitrogen found may be attributed to it.

On removal, the beans were found to possess much of their original firmness; but the other seeds, though retaining their form, were softer, and had evidently undergone more complete decomposition. Very little odour was emitted, and it was not unpleasant.

It is obvious that there had been no evolution of free nitrogen during the long period that these matters had been submitted to decomposition under the conditions described.

Experiments were also made upon the products of the decomposition of organic matter in the first stages of the process. The decomposition took place in water, in the tall glass vessels already described. In Table XVI are given the amounts, and the composition, of the gas obtained in a few out of numerous experiments; and, for comparison, some of the results already referred to are included.

TABLE XVI.

Description of Organic matter subjected to decomposition	Total gas collected.	Composition of the gas, per cent.		
		Carbonic acid.	Hydrogen.	Nitrogen.
	cub. cents.			
a. Wheat, Barley, and Bean seed ..	400	64·87	34·83	0·30
		64·54	35·46	traces.
b. Turnip plant; root with leaves.	166·2	76·23	22·91	0·87
c. Turnip plant; root with leaves.	162·2	68·83	23·93	7·24
d. Turnip plant; root with leaves.	123·6	68·06	25·63	6·31
		67·52	25·43	7·05
e. Turnip plant; root with leaves.	41·2	64·95	14 66	20·39

Experiment (*a*) is the one described above. In all the other cases, about two ounces of plant were operated upon. The experiment commenced on August 29, and was stopped on October 5, when the structure of the plant was almost entirely destroyed, there remained only a mass of decomposed matter at the bottom of the vessels, and the evolution of the gas had entirely ceased. The plant (*b*) was exhausted of its gas before exposure; and, under these circumstances, a very small quantity of free nitrogen was found at the termination of the experiment, whilst plants *c*, *d*, and *e*, which were not so exhausted, gave a larger amount of free nitrogen; and, although in experiment (*e*) the percentage of nitrogen was much higher than in the other cases, the total quantity of gas was much less, and the actual quantity of nitrogen was nearly the same in the several cases, leading to the supposition that it existed within the plant at the commencement of the experiment.

The result is, then, that, in the absence of free oxygen, no free nitrogen was evolved from the decomposing nitrogenous compounds, and it may be inferred that the loss of nitrogen indicated in Tables XIII and XV was the result of an oxidising process.

Some experiments were also made in which the plan was to place nitrogenous organic matter in an atmosphere of pure oxygen, and to afford a constant supply of the gas as it was consumed and the carbonic acid produced was absorbed by a solution of caustic potass. The results obtained indicated an evolution of free nitrogen; but owing to the difficulty of getting the requisite apparatus absolutely air-tight, they were open to some exception, and the investigation was, for the time, abandoned.

It is obvious that the results recorded point to a serious difficulty in the conduct of experiments on the question of the assimilation of free nitrogen by plants; for although, as Boussingault has shown, there may be no loss of nitrogen during germination, yet, during the entire period of growth of a plant, portions of nitrogenous organic matter may be subject to decomposition under conditions favourable to the evolution of free nitrogen.

The following experimental results are interesting in connexion with this point. Eight seeds, each, of wheat, barley, and oats, were respectively sown in prepared soil, precisely as in the experiments on assimilation. The three pots were placed under a glass shade, 16 inches in diameter, which rested in the groove of a stoneware lute-vessel containing sulphuric acid. About 500 cub. cent. of distilled water were added to each soil at the commencement, but no carbonic acid was supplied beyond that which might be contained in the water. The pots, enclosed as described, were then exposed to the diffused light of the laboratory, but without the access of direct sunlight. In a few days, all came up, and grew very rapidly in height, but with little development and expansion of leaf; all the plants being tall, slender, and delicate, and having the pale green colour common to plants in deficient sunlight. In other experiments, plants in this condition, when removed into sunlight, ceased the predominant upward tendency of growth, the long delicate first leaves lost their vitality, numerous shorter and broader ones were formed, and the stems became thicker and more dense.

The experiment under consideration commenced on May 17, 1858, and continued until June 10 (24 days), when the plants had ceased to grow. All the plants were much alike; ranging from 7 to 12 inches in height, each having three leaves, two lateral ones from 8 to 12 inches long, and a shorter, unrolled terminal one. The stems of several were so slender and delicate as to fall over. The roots were found to consist of short fibriles, with divaricated branchlets, seldom extending more than 2 or 3 inches from the seed. Table XVII gives the analytical results of the experiment:—

TABLE XVII.

Particulars of seed sown.			Particulars of the products.						
			Dry vegetable matter.			Nitrogen.			
	Dry matter.	Nitrogen.	Stems.	Roots.	Total.	In stems & roots.	In soil & pot.	In total products.	Gain or loss.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
Wheat	0·4077	·00790	·320	·140	·460	·00697	·0012	·00817	+ ·00027
Barley	0·3234	·00573	·290	·160	·450	·00570	traces	·00570	— ·00003
Oats..	0·2900	·00640	·355	·060	·415	·00640	traces	·00640	+ traces

Lest the accuracy of the result in regard to the nitrogen should be endangered, the roots were but slightly washed, and retained particles of soil, in consequence of which the weights given for their dry matter are a little too high. There was, however, evidently a slight gain of dry matter, the carbon of which was doubtless due to carbonic acid in the distilled water which had been supplied. The rapid growth, its short duration, the limited distribution of the roots, and the fact that no water was added during growth, which might distribute easily transportable matters, are conditions which are all consistent with the almost total absence of nitrogen in the soil.

The last column in the Table (XVII) shows that in these experiments no free nitrogen was given off during the process of germination and growth; at least the assumption that free nitrogen was evolved implies the still more improbable one that an exactly equal amount of free nitrogen was assimilated.

It would appear, therefore, that in an experiment on the question of the assimilation of free nitrogen by plants, little fear of loss of nitrogen, due to the decomposition of nitrogenous organic matter, need be entertained, so long as that matter is subjected to the ordinary process of germination, and exhaustion to supply materials for growth; though there may be considerable danger of such loss if nitrogenous organic matter were used as manure, or in case of the decomposition of sterile seeds, dead leaves, old roots, or nitrogenous excretions. In judging, according to the conditions of the assimilation experiment, of the probable extent of such evolution, it should be borne in mind that, in the cases where the large evolution of free nitrogen took

place in the experiments on decomposition, the organic matters were subjected to the action for a period of about six months, during which time their organic form was generally entirely destroyed, and they lost nearly three-fourths of their carbon.

One more collateral point requires to be noticed before entering upon the consideration of the direct experiments on the question of assimilation.

Results quoted above leave no doubt of the evolution of hydrogen during the decomposition of organic matter, and Mulder,* and others, have attached much importance to the mutual action of nascent hydrogen so evolved, and gaseous nitrogen, as a source of ammonia. That nascent hydrogen may, under certain circumstances, combine with gaseous nitrogen, has long been admitted; but the view that such combination takes place when hydrogen is evolved from decomposing organic matter, requires confirmation. If but a small part of the hydrogen evolved in the decomposition of organic matter in peat-bogs, in cesspools, in stagnant water, in the annual deposits of leaves in the extensive forests in different parts of the world, decaying under the influence of moisture and confined air between the succeeding layers, as well as in many soils, were to combine with free nitrogen, how enormous would be the amount of ammonia formed in this way—the amount due alone to the decomposition of the exuberant growth of former geological periods would be incalculable.

The results which have been given show, that in the decomposition of nitrogenous organic matter, both free hydrogen and free nitrogen may be given off; and the assumption that nascent hydrogen under such circumstances unites with the nitrogen of the air, implies that it was capable of uniting with free nitrogen under circumstances in which its affinities were not sufficiently powerful to prevent nitrogen-compounds, very similar to ammonias, from giving up nitrogen in the free state; and also that it could act upon ordinary nitrogen when it could not do so upon the nascent nitrogen of the decomposing nitrogenous body. Or, if it did act upon the latter, there would either be no free nitrogen evolved, or if there were, it would show that less nascent nitrogen had been converted into ammonia than had had been liberated from its combinations, the result of which would be a loss, and

* Chemistry of Vegetable and Animal Physiology, pp. 111–114, 149–152, &c.

Fig. 1.

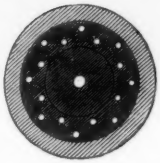


Fig. 2.

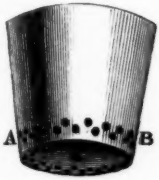


Fig. 3.

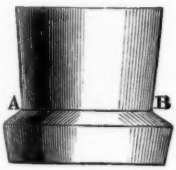


Fig. 4.

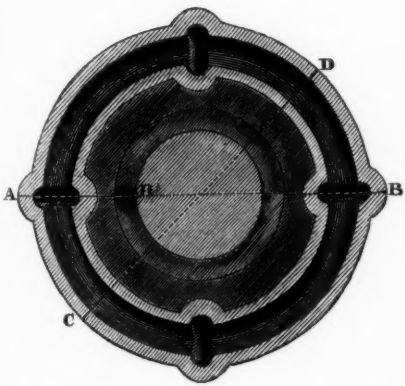


Fig. 5.

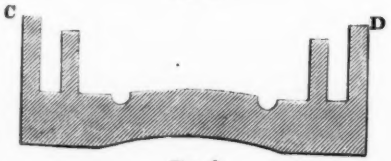


Fig. 6.

Fig. 7.

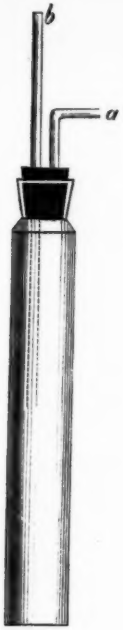


Fig. 8.

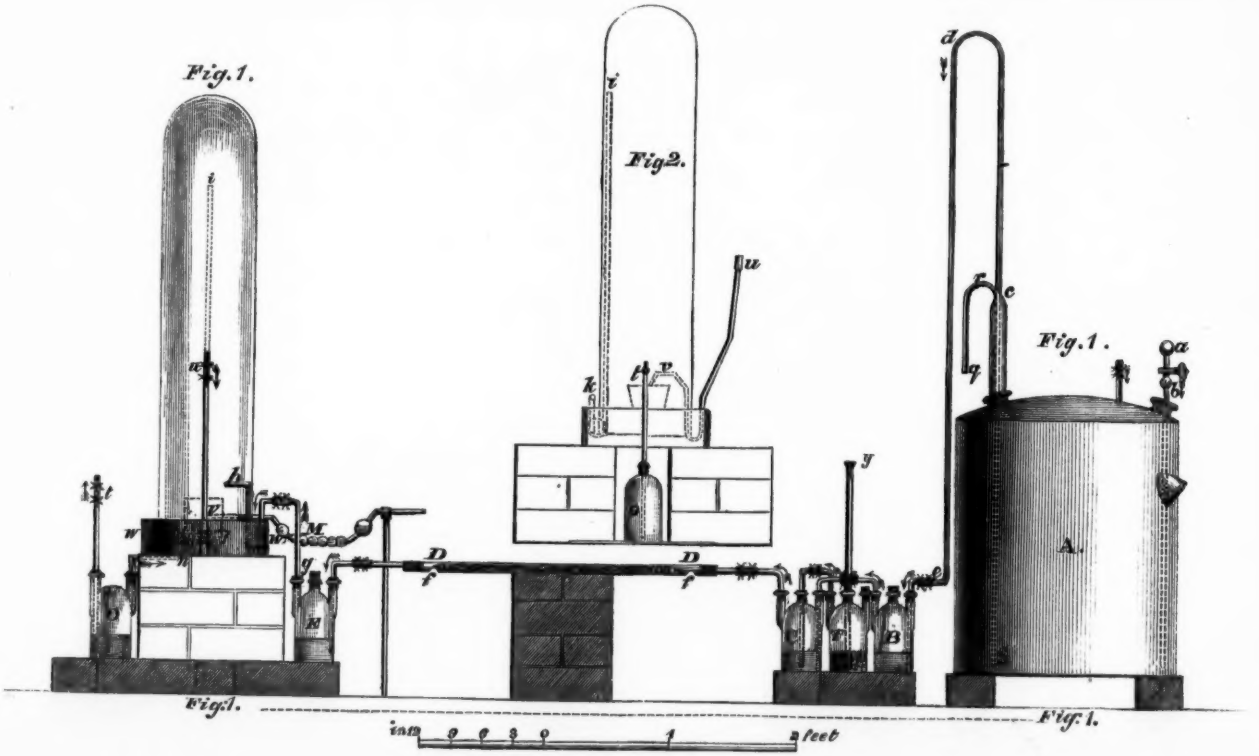


PLATE II.

Supplied with no other combined Nitrogen

Fig. 1.

Wheat – 1857
in prepared soil.

Fig. 2.

Barley – 1857
in prepared soil.

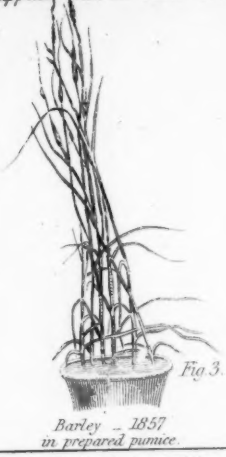


Fig. 3.

Barley – 1857
in prepared pumice.

Wheat –
in prepare

Supplied with known and limited quantities of combined

Fig. 7.

Wheat – 1857
in prepared soil.

Fig. 8.

Barley – 1857
in prepared soil.

Fig. 9.

Barley – 1857
in prepared pumice.

Wheat
in prep

Scale 1/3

Nitrogen than that contained in the seed sown.

Fig. 4

Wheat – 1858
in prepared soil.

Fig. 5.

Barley – 1858
in prepared soil.

Fig. 6.

Oats – 1858
in prepared soil.

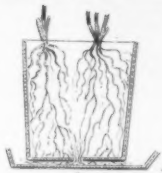


Fig. 14.

Fig. 15.

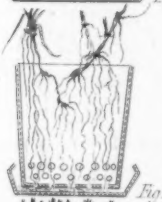


Fig. 16.

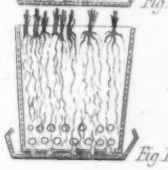


Fig. 17.

bined. Nitrogen beyond that contained in the seed sown.

Fig. 10.

Wheat – 1858
in prepared soil.

Fig. 11.

Barley – 1858
in prepared soil.

Fig. 12.

Oats – 1858
in prepared soil.

Fig. 13.

Wheat Barley & Beans – 1857
in Garden soil.

Scale 1 to a foot.

J. Basire Sc.

not a gain of combined nitrogen. But the fact is that both free hydrogen and free nitrogen are given off.

It would seem from the above considerations, that there need be little apprehension of error in the results of experiments on the question of assimilation, arising from an unaccounted supply to the plants of ammonia formed under the influence of nascent hydrogen given off in any decomposition of the organic matter involved in the experiment.

Having described the arrangement adopted in our experiments on the question of the assimilation of free nitrogen by plants, and discussed some collateral points, particularly those which relate to the possible sources of gain or loss of combined nitrogen to the plants under experiment, it only remains further to preface the statement of the experimental results obtained, by considering what are the most probable conditions for the assimilation of free nitrogen, provided it can take place at all?

The questions arise—whether such assimilation would be most likely to take place, when the plant had no other supply of combined nitrogen than that in the seed sown, when supplied with a limited amount of combined nitrogen, or with an excess of combined nitrogen? And again—whether at an early stage of growth, at the most active stage, or when the plant is approaching maturity? Combinations of these several circumstances might give a number of special conditions, in perhaps but a few of which assimilation of free nitrogen could take place, if in any.

It would hardly be supposed that free nitrogen would be assimilated when an excess of combined nitrogen was at the disposal of the plant. It is obvious, however, that a wide range of conditions would be experimentally provided, if, in some instances plants were supplied with no more combined nitrogen than that contained in the seed sown, in others they were brought to a given stage and activity of growth by means of limited extraneous supplies of combined nitrogen, and in others the supply of combined nitrogen were still more liberal. It has been sought to provide these several conditions in the experiments under consideration. In either case supposed above, the plant will, at a certain stage, or at certain stages, as the case may be, have an excess of combined nitrogen at its disposal in relation to its immediate wants, and will pass from this point through all stages in regard to supply, to that in which combined nitrogen is in defect. If, how-

ever, the plant cannot assimilate free nitrogen unless it has attained a certain vigour or stage of growth, it may, perhaps, be alleged, in case of no assimilation taking place, that the supply of combined nitrogen has been insufficient to bring it to the supposed point; but if, on the contrary, the assimilation can take place at all periods of growth, and in the absence of all extraneous sources of combined nitrogen, the solution of the question becomes much more easy. Indeed, even in an experiment without any extraneous supply of combined nitrogen, all the conditions with regard simply to the relative quantity of combined nitrogen, are provided. Thus, when the seed is first sown, it contains within itself an excess of combined nitrogen so far as the immediate wants of the plant are concerned, and it will gradually pass to the point at which all available combined nitrogen has been appropriated, and only free nitrogen is presented to it. A negative result under such circumstances even, would afford evidence against assimilation of free nitrogen under a wide range of conditions; and a similar result with various amounts of combined nitrogen supplied, would be conclusive as to a still wider range of circumstances of growth.

The last point for consideration is as to the selection of the plants to submit to the adopted conditions of the experiment. It was sought—(1) to have such as would be adapted to the conditions of temperature, moisture, &c., to which they were to be subjected; (2) to have such as were of importance in an agricultural point of view; (3) to acquire the means of studying any difference, in reference to the point in question, between plants belonging, respectively, to the two great natural orders, the Graminaceæ and the Leguminosæ, which, in some points of view, appear to differ so widely in their demands upon combined nitrogen provided within the soil; (4) to take such as had already been experimented upon, with such conflicting results, by M. Boussingault and M. G. Ville.

Experiments in which the Plants had no other supply of Combined Nitrogen than that contained in the Seed sown.

Table XVIII, p. 172, gives, at one view, a summary of the numerical results obtained under this head; see also figs. 1—6, plate III, which are reduced from careful drawings of six out of the nine Graminaceæ experimented upon, and illustrate the

character and extent of growth attained under the conditions in question.

After so full a discussion of the circumstances under which the results were obtained, but little more is needed in pointing out their bearings upon the question at issue, than to direct attention to the column showing the gain or loss in each experiment.

The differences between the results obtained with soil and with pumice as matrix, in 1857, are not such as can be attributed in any way to the difference of matrix; indeed, the parallel experiments with the two descriptions of soil may be considered as duplicates.

Graminaceous Plants.

It is seen that the largest gain of nitrogen in the three experiments with Graminaceæ, in 1857, was 0·0026 gramme. In regard to the fact that there was generally a somewhat larger gain of nitrogen in some of the experiments in 1857 than in those in 1858, it may be observed that, soon after watering with the fluid drawn off from the surface of the slates used in the former year as lute-vessels, the soils in one or two cases became more or less covered with a slight coating of green matter. And nearly all the slates were found at the end of the experiment to have a similar coating beneath the pans in which the pots stood; whilst, in the experiments of 1858, when glazed earthenware lute-vessels were employed, no such phenomenon was observed. Keeping in view this fact, and considering that so small an amount of nitrogen had to be determined in so large an amount of soil (0·003 gramme or less of nitrogen in about 1,500 grammes of soil), it seems more than questionable whether the small gain above quoted, should not be attributed to errors of experiment or analysis. In fact, we can but conclude, that under the circumstances of growth of the Graminaceous plants to which Table XVIII relates, there has been no assimilation of free nitrogen. There is, indeed, in no case more nitrogen in the plant itself than in the original seed, the gain appearing only when that in the soil and pot is taken into account.

The experiments on germination and growth referred to at pp. 166–7, showed how completely the plants could appropriate the nitrogen of the seed, leaving only traces in the soil; and the experiments on decomposition showed how complete was the action coincident with the passage of any large proportion of the

TABLE XVIII.

Results of Experiments to determine whether Plants supplied with no combined Nitrogen beyond that in the Seed sown, assimilate free Nitrogen.

Years.	Plants.†	Number of seeds. Sown.	Number of seeds. That grew.	Period of growth.	Dry substance. Grammes. In seed.	Dry substance. Grammes. In plants produced.	Dry substance. In produce to that in seed sown taken as 1.	Nitrogen. Grammes. In seed.	In total plant.	In soil.	In pot.	In condensed water.	In total products.	Gain or loss.	Nitrogen. In plants to 100 in seed sown.	Nitrogen. Per cent. in dry produce.
Graminaceæ.																
1857	Wheat (1)	6	5	May 16—Oct. 3	0·3065‡	1·412	4·61	·0080	·0072	traces	traces		·0072	– ·0008	90·0	0·51
1857	Barley (2)	6	6	May 20—Aug. 24	0·2698	0·810	3·01	·0056	·0047	·0024	·0001		·0072	+ ·0016	83·9	0·58
1857	Barley (3)	6	6	May 20—Aug. 25	0·2698	0·925	3·43	·0056	·0045	·0030	·0007		·0082	+ ·0026	80·4	0·48
1858	Wheat (4)	8	8	April 27—Oct. 25	0·4035	1·740	4·31	·0078	·0056	·0025		traces	·0081	+ ·0003	71·8	0·32
1858	Barley (5)	8	6	April 27—Aug. 18	0·3221	0·560	1·74	·0057	·0031	·0027		traces	·0058	+ ·0001	54·4	0·54
1858	Oats (6)	8	8	April 27—July 13	0·2858	1·148	4·02	·0063	·0042	·0011		·0003	·0056	– ·0007	66·7	0·36
1858, A*	Wheat	8	7	June 11—Nov. 6	0·4031	1·060	2·63	·0078	·0041	·0033		·0004	·0078	0000	52·6	0·38
1858, A*	Barley	8	8	June 11—Nov. 6	0·3240	0·710		·0057								
1858, A*	Oats	8	7	June 11—Nov. 6	0·2879	0·690	2·40	·0064	·0038	·0021		·0004	·0063	– ·0001	59·4	0·55
Leguminosæ.																
1857	Bean	2	2	May 16—July 5	1·4984	7·028	4·69	·0796	·0629	·0146	·0016		·0791	– ·0005	79·0	0·89
1858	Bean	3	3	June 11—Aug. 23	1·4820	4·875	3·29	·0750	·0735	·0016		·0006	·0757	+ ·0007	98·0	1·51
1858	Pea	3	3	June 5—Aug. 24	0·5405	0·970	1·79	·0188	·0102	·0056		·0009	·0167	– ·0021	54·3	1·05
Other Plants.																
1858	Buckwheat	24	13	Aug. 20—Oct. 28		0·450		·0200	·0070	·0108		·0004	·0182	– ·0018	35·0	1·56

* These experiments were conducted in the apparatus of M. G. Ville.

† The numbers given in brackets refer to those of the figures of the respective plants given in Plate III.

‡ The percentage of dry matter in the seed was not determined in this case; it is therefore assumed to be the same as in the wheat used in 1858, from which it would certainly not differ at all materially.

nitrogen of the substance into the soluble state of ammonia. It would appear probable, therefore, that at least a part of the nitrogen found in the soil had never been in actual connexion with the plant; and it must be admitted, that a gain in the total products, without a gain in the plant itself, would, under the conditions in question, be unsatisfactory evidence of the assimilation of free nitrogen.

The results obtained with Graminaceæ in 1858, when some sources of error which the experience of the previous year had suggested had been eliminated, point, without exception, to the non-assimilation of free nitrogen. The process of cell formation has gone on; carbonic acid has been decomposed, and carbon and the elements of water assimilated; the nitrogenous compounds of the older cells have been withdrawn for the requirements of new ones; the roots, requiring the smallest amount of nitrogen, were extraordinarily developed; and all stages of growth have been passed, to the formation of glumes, pales, and awns, for seed, the other organic constituents increasing with one constant amount of combined nitrogen until its percentage in the vegetable matter was far below the usual amount. Throughout these phases, water saturated with free nitrogen has constantly been in contact with the contents of the cells and the cell-walls; the delicate membrane of the newly-forming cell, stunted in its development for want of assimilable nitrogen, has been saturated with water, itself saturated with free nitrogen; and such are the laws in accordance with which the absorption of gases, and the transmisson of liquids through membranes take place, that the instant a part of the nitrogen became assimilated the equilibrium would be restored and the liquid resaturated, circumstances which would seem highly favourable to the assimilation of free nitrogen, provided it could take place at all.

In the experiments of 1857, several of the cereal plants developed a very large proportion of root, but fearing the double risk of losing the entire results in analysing the root and the rest of the plant separately, they were thoroughly mixed, and the mixture carefully divided, so as to provide confirmatory evidence if successful, or a duplicate in case of accident. The development was, however, so marked in the cereals of 1858, that the root was in several cases analysed separately. Table XIX shows the results obtained :—

‡ The percentage of dry matter in the seed was not determined in this case; it is therefore assumed to be the same as in the whole seed in 1857, from which it would certainly not differ at all materially.

TABLE XIX.

Plants.* (1858).	Dry matter.				Nitrogen.			
	In stems, &c.	In roots.	In total plant.	Per cent. of total in roots.	In stems, &c.	In roots.	In total plant.	Per cent. of total in roots.
	grm.	grm.	grm.		grm.	grm.	grm.	
Wheat (4) .	0·890	0·850	1·740	48·85	0·0039	0·0017	0·0056	30·36
Barley (5) .	0·400	0·160	0·560	28·57	0·0027	0·0004	0·0031	12·90
Oats (6) ..	0·798	0·350	1·148	30·49	0·0040	0·0002	0·0042	4·76

The large proportion of root, and its small proportion of nitrogen are equally remarkable. Whether the great development of root were due to the process of cell formation in it requiring less of the nitrogenous proto-plasmic compound, or to the withdrawal, by the fluid in which the roots floated, of the nitrogenous constituents from the old cells to form new proto-plasma for the more active cells, is a question of considerable interest in a physiological point of view. The fact that the roots gave off very few branches into the soil, but immediately on reaching the water in the pan exhibited such a remarkable development, is in favour of the inference that the water afforded the necessary conditions.

At any rate, this great development of the part of the plant requiring a minimum of nitrogen indicates an inability to assimilate free nitrogen within the range of growth possible when no combined nitrogen is provided beyond that in the seed sown; and it shows the great tenacity of growth, and activity of vital force, long after the organism began to require more available nitrogen—conditions apparently very favourable to the assimilation of free nitrogen; yet such has not been the result.

The Graminaceæ referred to in Table XVIII. under the title "1858 A," which were grown in M. G. Ville's case, give results perfectly accordant with the rest; but being sown later, and their period of growth being shorter, there was neither so great a development of root nor so much total vegetable matter produced. Unfortunately, the barley of the series was lost by the giving way of the tube in combustion; so that, in its case, we can only give the amount of dry matter produced; but, comparing the

* The numbers given in brackets refer to those of the figures of the respective plants given in plate III.

results on this point with those in the other cases, there is no reason to believe that those in regard to the nitrogen would have been different.

It will be remembered that M. Boussingault and M. G. Ville obtained most discordant results in experimenting with Graminaceæ, and it will be seen that our own results, from nine experiments with such plants, go entirely to confirm those of M. Boussingault.

Leguminous Plants.

It has been shown in section 1 of this paper, that, under equal circumstances of soil and season, Leguminous crops yield two, three, or more times as much nitrogen per acre, as Graminaceous ones; that, nevertheless, the latter are very characteristically benefited by the direct use of ammoniacal manures, whilst the former are not so; and again, that a much larger Graminaceous crop is obtained after the growth and removal of a highly nitrogenous Leguminous one, than after another Graminaceous crop. Experiments such as those now under consideration, can obviously bear upon a few only of the circumstances which may be connected with the differences referred to. They do, however, bear upon the questions—(1) whether in the growth of the Graminaceæ, there is a decomposition of nitrogenous compounds and an evolution of free nitrogen? or, (2) whether the Leguminosæ may assimilate free nitrogen, and thus not only allow the resources of the soil to accumulate, but leave within it, in roots and other vegetable *débris*, an additional quantity of combined nitrogen?

The facts already considered do not indicate an evolution of free nitrogen from the nitrogenous compounds of Graminaceous plants during growth; and others, to which we shall presently refer, afford confirmatory evidence in the same direction.

With regard to the second point, as the growth of the Leguminous plants under the experimental conditions was generally not so healthy as that of the Graminaceæ, it may, perhaps, be maintained, that a negative result with them was not so conclusive as with the latter. In 1857, several experiments with beans were commenced, but they grew well in only one of the shades. These, however (especially one plant out of the two in the same pot), progressed remarkably well for 10 weeks, during which time the amount of dry matter, and consequently of carbon, increased

about five-fold; more than three-fourths of the nitrogen of the seed was appropriated, and the plants probably ceased to grow only when the remainder became so distributed in the soil as not to be available. The beans and peas of 1858 did not grow so satisfactorily as the beans of 1857 last referred to; yet the beans (of 1858) gave more than three times as much organic matter in the produce as was contained in the seed, and appropriated even a much larger proportion of the nitrogen of the seed than did those of 1857. The result with the peas was not so satisfactory, owing to the less healthy and more limited character of the growth. It may be added that none of these Leguminous plants arrived at the stage of flowering.

The result is, however, that active growth has taken place—that the process of cell formation, with the decomposition of carbonic acid and fixation of carbon, has gone forward with a deficient supply of combined nitrogen, and in the immediate presence of free nitrogen, both gaseous and dissolved—in fact, that the plants have been subjected to a considerable range of the conditions which appear, *à priori*, to be favourable to the assimilation of free nitrogen, yet none has been assimilated by these Leguminous plants any more than by the Graminaceous ones.

It is a fact observed in agriculture, that manures rich in organic matter, frequently favour the growth of Leguminous crops; and without discussing the question whether they act as a source of carbonic acid merely, or of carbon-compounds of a more complicated character, attention may be called to the fact, that, in the experiments now under consideration, the vital forces were sufficiently energetic to perform the function of cell development and multiplication, from carbonic acid as the source of carbon, and yet they were incapable of effecting the appropriation of free nitrogen.

Buckwheat.

In the experiment with buckwheat, most of the seed sown came up, but about half of the plants lived only for a few days. The remainder went through all the stages of development to flowering, but the amount of growth was nevertheless very limited, the quantity of dry matter produced being less than that in the seed sown, and the nitrogen in the plants little more than one-third that in the seed. It will be seen further on, however, that on the addition of an amount of ammonia very small in its contents of

nitrogen compared with the seed, to plants in a precisely similar condition to those now under consideration, the increase of growth was extremely marked.

Reference to the column in Table XVIII. giving the gain or loss of nitrogen, will show that, under the conditions of growth described, there was no gain of nitrogen by the buckwheat, but on the contrary a loss of nearly 2 milligrammes, doubtless due to the evolution of free nitrogen in the decomposition of some of the plants that died.

Various experimenters, from the time of De Saussure, have entertained the idea of the probability of the decomposition of nitrogenous compounds, and the evolution of free nitrogen, during the growth of plants. We have been engaged in following up the subject in a more direct manner, but attention may here be called to the incidental bearing upon it of the results above considered.

With no less force than they point to the non-assimilation of free nitrogen, do they show that there has been no evolution of free nitrogen from the nitrogenous compounds of the growing plant. At all events, from the constancy of the amount of combined nitrogen maintained in relation to that supplied, the assumption that an evolution has taken place, implies the still more improbable one, that there has been an exactly compensating assimilation. But, when supplied with an insufficient quantity of nitrogenous matter, the vegetable organism might not decompose any of that matter; and yet, with an excess of combined nitrogen, decomposition might take place. We shall, therefore, refer to this question again, in connexion with the results obtained when an extraneous supply of combined nitrogen was provided to the plants.

Experiments in which the Plants had a known supply of Combined Nitrogen beyond that contained in the Seed sown.

Although in the experiments already considered, the extent of growth was very limited, some of the cereals did indeed produce glumes and pales for seed; but none attained to the formation and ripening of the seeds themselves. It remains to consider, therefore, what may take place with more active and vigorous growth, and at a later stage of development.

We have suggested the improbability of an assimilation of free nitrogen taking place in the presence of an abundance of combined nitrogen; but if active, healthy, and vigorous growth are favourable to the assimilation of free nitrogen, and these conditions can only be attained by keeping within the reach of the plant an excess of combined nitrogen, we should have to conclude that free nitrogen could be taken up in the presence of, and in preference to, combined nitrogen; *à priori* conclusions on points involving vital phenomena are, however, obviously unsafe.

It is true, we have pointed out the improbability of an assimilation of free nitrogen in the presence of an excess of combined nitrogen, only so far as the vital process of the vegetable cell is concerned. But, the more active the growth, the greater must be the amount of newly-formed carbon-matter capable of consuming oxygen when the plant is removed from the influence of sunlight into the dark. That is, the more vigorous the growth in the sunlight, the greater may be the reducing power of the plant in the dark; and the greater this reducing power, the more nearly will the tendency of the forces approximate to an evolution of hydrogen, which, in the presence of free nitrogen dissolved in the fluids of the cell, may tend to form ammonia, to be, on the return of sunlight, appropriated by the plant. In connexion with this point, it may be mentioned that in our investigation of the gases given off by plants under various circumstances, we have had an evolution of oxygen one day as a coincident of growth, and an evolution of hydrogen the next, as the result of decomposition.

The results of the experiments in which the plants were supplied with combined nitrogen beyond that in the seed sown, are given in Table XX, p. 179; and the figures 7—12, plate III, show the character and extent of development of six Graminaceous plants with extraneous supply of combined nitrogen, corresponding to the six above them without such supply; and the vigour and extent of growth attained, may be taken as sufficient proof that the conditions of soil, atmosphere, temperature, &c., were consistent with active and healthy growth. As already explained, the combined nitrogen was supplied by means of dilute solutions of sulphate of ammonia.

It will be instructive to consider the results to which Table XX refers, in regard—(1) to the actual gain or loss of nitrogen; (2) to the physiological evidence afforded during growth; (3) their indications as compared with the results obtained when there

TABLE XX.

Results of Experiments to determine whether Plants supplied with combined Nitrogen beyond that in the Seed sown, assimilate free Nitrogen.

Years.	Plants.†	Number of seeds. Sown.	Number of seeds. That grew.	Period of growth.	Dry substance. Grammes. In seed.	Dry substance. Grammes. In plants produced.	Dry substance. In produce to that in seed sown taken as 1.	Dry substance. In produce per seed with ammonia, to that without it taken as 1.	Nitrogen. Grammes. In seed.	In manure.	Total supplied	In total plant.	In soil.	In pot.	In condensed water.	In total products.	Gain or loss.	Nitrogen. In plants to 100 in seed and manure.	Per cent in dry produce.	Nitrogen. In produce per seed with ammonia, to that without it taken as 1.
Graminaceæ.																				
1857...	Wheat (7)...	3	2	May 16—Oct. 2 ...	0·1536‡	6·835	44·50	12·10	·0040	·0289	·0329	·0241	·0133	·0009		·0383	+ ·0054	73·3	0·35	8·36
	Wheat	3	3	May 16—Sept. 20 .	0·1543‡	3·822	24·79	4·51	·0040	·0289	·0329	·0213	·0102	·0016		·0331	+ ·0002	64·7	0·55	4·93
	Barley (8)...	4	3	May 20—Oct. 8 ...	0·1803	3·034	16·83	7·49	·0037	0289	·0326	·0154	0171	·0003		·0328	+ ·0002	47·2	0·51	6·58
	Barley (9)...	4	4	May 20—Sept. 24 .	0·1818	4·401	24·18	7·13	·0037	·0231	·0268	·0145	·0171	·0021		·0337	+ ·0069	54·1	0·33	4·83
1858...	Wheat (10) .	4	4	April 27—Oct. 26 .	0·204	7·31	35·83	8·40	·0040	·0508	·0548	·0398	·0138		traces	·0536	— ·0012	72·6	0·54	14·21
	Barley (11) .	4	2	April 27—Oct. 26 .	0·158	5·47	34·62	29·31	·0028	·0468	·0496	·0349	·0113	·0002		·0464	— ·0032	70·4	0·64	34·21
	Oats (12) ...	4	3	April 27—July 30 .	0·145	1·204	8·31	2·80	·0032	·0280	·0312	·0125	·0040	·0051		·0216	— ·0096	40·1	1·04	7·92
1858, A*	Wheat	4	4	June 29—Dec. 9...	0·206	3·82	18·54	6·31	·0040	·0228	·0268	·0181	·0092	·0001		·0274	+ ·0006	67·5	0·47	7·79
	Barley	4	3	June 29—Dec. 9...	0·162	2·98	18·40		·0029	·0228	0257	·0160	·0081	·0001		·0242	— ·0015	62·3	0·54	
	Oats	4	2	June 29—Dec. 9...	0·144	1·28	8·89	6·49	·0032	·0228	·0260	·0146	·0051	·0001		·0198	— ·0062	56·1	1·14	13·52
Leguminosæ.																				
1858...	Pea	3	3	April 27—Aug. 24.	0·539	1·01	1·87		·0187	·0040	·0227	·0114	·0086	·0011		·0211	— ·0016	50·2	1·13	
	Clover			June 6—Oct. 26 ...		4·20			·0284	·0428	·0712	·0313	·0339	·0013		·0665	— ·0047	44·0		
858, A*	Bean	3	3	June 29—Dec. 9...	1·094	4·30	3·93		·0523	·0188	·0711	·0401	·0253	·0001		·0655	— ·0056	56·4	0·93	
Other Plants.																				
1858.....	Buckwheat.	42	24	Aug. 20—Nov. 22.	0·850	1·97	2·32	2·37	·0200	·0108	·0308	·0183	·0101		·0008	·0292	— ·0016	59·4	0·92	1·41

* These experiments were conducted in the apparatus of M. G. Ville.

† The numbers given in brackets refer to those of the figures of the respective plants given in Plate III.

‡ The percentage of dry matter in the seed was not determined in these two cases; it is therefore assumed to be the same as in the wheat used in 1858, from which it would certainly not differ at all materially.

was no other supply of combined nitrogen beyond that in the seed sown.

As in the experiments without, so also in those with a supply of combined nitrogen beyond that in the seed sown, there is generally a slight gain of nitrogen in those of 1857, but almost invariably a loss rather than a gain in those of 1858, when glazed stone-ware, instead of slate lute-vessels were employed; and considering the possible source of gain when slates were used, the whole of the results can be interpreted but in one way.

The slight loss of nitrogen in the experiments of 1858 is easily accounted for. The general character of growth of the peas, clover, and beans, under the experimental conditions, as already referred to, taken in connection with the evidence adduced as to the loss of nitrogen during the decomposition of nitrogenous organic matter, sufficiently explains the loss in their case. The loss in the cases of the wheat, barley, oats, and buckwheat (1858), would not be so easily explained, had not the combined nitrogen in the drainage-water remaining at the end of the experiment been determined separately; and the fact that a notable quantity of ammonia was found in the condensed water, only where there was a *loss* of combined nitrogen in the experiment, would lead to the inference, that both phenomena were due to the same cause.

The condensed water showing the amounts of combined nitrogen recorded in the table, was that collected during the last four weeks of growth; and during this period the high temperature, and the advanced stage of growth of the plants, were favourable to the evaporation of ammoniacal water. Owing to the comparatively low temperature of the shade, a large proportion of the vapour would condense on its interior, and finally be collected in the bottle O; but a certain quantity of that present in the atmosphere of the apparatus, during the passage of the air through it, would be borne forward into the sulphuric acid in the bulb-apparatus M, and thus occasion a loss of combined nitrogen. The reason of the greater loss in both the experiments with oats, than in those of the other cereals, is not perfectly obvious; but in connection with this point it may be mentioned that, in one case more particularly, they ripened at a much warmer period of the season, and becoming much drier in stem and leaf, might be more liable to evolve ammonia.

It is, however, not enough to consider the actual gain or loss of nitrogen merely, but it is desirable to take into account the total

quantity of nitrogen at the disposal of the plants, and also the amount and character of growth, under the different conditions, or, in other words, the physiological evidence.

We have already called attention to the fact of the very great increase of growth when a supply of combined nitrogen, extraneous to that of the seed sown, was provided. This is strikingly illustrated by the figures in the columns of Table XX, which show the amounts respectively, of dry substance and of nitrogen, in the final produce per seed with ammonia to that without it taken as 1; but the indications manifested from the earliest periods of growth require to be briefly noticed.

When they first came up, all the plants looked green and vigorous, indicating the presence of all conditions essential to healthy growth; and there can be little doubt that, at that time, they were supplied with an excess of combined nitrogen in relation to their immediate wants. After some days, varying with the nature of the plants, they began to assume a lighter green or pale yellow tint, indicative of a want of combined nitrogen. It has been already pointed out how favourable, probably, would be the condition for the assimilation of free nitrogen, when the plant was passing from the state in which it had an excess to that in which it had a deficiency of combined nitrogen for the demands of growth. The vigorous development of the plants grown under the same conditions as the other experimental plants, but in garden soil (fig. 13, plate 3), indicates that the conditions of atmosphere, &c., provided, were not at fault. If a supply of combined nitrogen alone be deficient when the plants show the declining vigour above described, they will, on its addition, resume their healthy green colour. Or, if combined nitrogen be added before the plants decline, it will prevent them assuming the pale green or yellow colour. Both these expedients have been adopted; and so far as the cereals, buckwheat, and clover are concerned, each has yielded a result indicating that combined nitrogen alone was needed for healthy growth.

The plants to which ammonia was given in 1857, were allowed to suffer more before they received it, than those of 1858; yet in thirty-six hours after its addition to the soil, in amount not exceeding 1·5 milligramme of nitrogen to each plant, they began manifestly to improve, and in two or three days the effect was quite marked; but at the termination of periods varying from nine to eighteen days, they seemed to have consumed all that had

not become inaccessible in the soil, and began to show the same indications of defective supply as before. A new increment of combined nitrogen (excepting when in one or two instances it was added too late) caused a new increment of growth, greener colour, and a more vigorous appearance generally, to be soon followed by the recurrence of the pale colour, and so on. At each recurrence of these conditions, the plants must have passed, at a more advanced stage of growth than before, from the point of having an excess to that of having a deficiency of combined nitrogen.

A considerable range of conditions of growth was thus provided. Just after each addition, the plants must have been supplied with an excess of nitrogen in an available form, as was evinced in the formation of new shoots from the base or the nodes of the plants. But these new shoots, at first growing vigorously, soon suffered for want of a new supply; and in passing to this point, the newly-formed and vigorously-growing portion of the vegetable matter, would be in the condition assumed to be the most favourable to the assimilation of free nitrogen. This cycle of conditions, repeated several times during the growth of the same plant, and the experiment similarly conducted with a number of pots of plants of different kinds, with like results in all cases, afforded a wide range of circumstances assumed to be favourable to the assimilation of free nitrogen, which, however, has not taken place.

Table XX shows, that there remained in the soil, at the termination of the experiment, a greater or less amount of the combined nitrogen artificially supplied, yet the physiological evidence sufficiently showed the effect of each new addition; nor is it difficult to imagine that a few milligrammes of ammonia, intermingled with 1,500 or 1,600 grammes of soil (and pot), might become so distributed and absorbed, that a considerable proportion should remain inaccessible to the plant.

The Graminaceous plants of 1858 were supplied with combined nitrogen at an earlier period of growth than those of 1857, and were not allowed to show such marked signs of deficiency before receiving fresh supplies.

Attention should be called, in passing, to the remarkable character of growth exhibited in some of the experiments.

Shortly after the addition of ammonia to the Graminaceæ for the first time, the plants began to throw out new shoots from the base of the principal stem, as if they had first developed a stem commensurate with the limited amount of combined nitrogen con-

tained in the seed, and then, with the new supplies, been obliged to find vent for their activity in new directions. Some of the new shoots came forth close to the surface of the soil, some at the first, and some at the second nodes, as the drawings of the plants, given in plate 3, will show.

Another remarkable feature was the formation of roots at the second and third nodes above the ground, in the case of most of the Graminaceæ to which ammonia-salt was added. These roots came out around the node, and extended downwards, several reaching the soil from heights varying from $\frac{1}{2}$ to $1\frac{1}{2}$, or even 2 inches, and penetrating it to the bottom of the pot. The most marked instance was that of the barley, fig. 11, plate 3, given in more detail with special reference to these points, in fig. 16, plate 3. As the figures show, roots and new stems came from the same node, making the latter a new axis of growth, like the seed in the first instance. The original stems, below these nodes, did not increase much in size with the addition of ammonia, but the stems above the nodes became much larger than the portions below them, as did those of the new shoots.

Finally, in regard to the Graminaceæ: so long as an additional supply of combined nitrogen increased growth, so long must the physiological conditions have required available nitrogen, and therefore have been more or less favourable to the assimilation of free nitrogen if this were possible; but no such assimilation took place.

With regard to the other plants little more need be said than to direct attention to the columns of gain or loss of nitrogen. As already observed, the growth of the Leguminosæ was by no means so satisfactory as that of the Graminaceæ; and hence, the results relating to them apply to a more limited range of conditions of growth, and are, therefore, less conclusive against the possibility of the assimilation of free nitrogen in their case; though, so far as they go, they, as well as those with the buckwheat, tend to confirm those with the cereals. It should be remembered, too, that M. Boussingault experimented with a great many Leguminous plants, and generally succeeded in getting much more healthy growth than we were able to do, but in no case did he find any such gain of nitrogen as to lead to the conclusion that free nitrogen had been assimilated. We shall, ourselves, have additional evidence to bring forward on this subject on a future occasion.

In regard to the single experiment with clover, the results of which are given in Table XX, it may be mentioned that we failed

to get any growth in the experiment attempted without the addition of ammonia, and obtained comparatively little with it. Beans and peas also proved so sensitive under the conditions of experiment, and were so much less characteristically benefited by the supply of ammonia-salts, that it was obvious they suffered from other causes than a want of combined nitrogen. In subsequent experiments, however, nitrates have been found to be much more beneficial than ammonia-salts; as, indeed, they are when applied to Leguminous crops grown in the field.

It has already been pointed out that the beans grown in 1857 without extraneous supply of combined nitrogen, appropriated nearly four-fifths, and those grown in the same way in 1858 a larger proportion still, of the nitrogen of the seed sown. In contrast with these results, it may be mentioned that, in the experiment with beans, "1858 A" (see Table XX), there were 0·0523 gramme of nitrogen in the seed sown, and 0·0188 gramme supplied as ammonia-salt, making together 0·0711 gramme, of which the plants appropriated only 0·0401 gramme, or about one-fifth less than was supplied in the seeds alone; yet, it was in this experiment with Leguminous plants, that the addition of ammonia-salt produced the most obvious effects on the growth.

From a review of the whole of the results of the direct experiments on the question of assimilation, it appears that the Graminaceous plants grew the most healthily, and provided a wide range of conditions for the assimilation of free nitrogen; that the Leguminous plants were less healthy, and therefore provided a more limited range of conditions for assimilation; and that the growth of other plants was also less satisfactory than that of Graminaceous ones. In all, the growth was more or less increased by the supply of combined nitrogen beyond that contained in the seed. The effect was the most marked with the Graminaceous plants, their increase of dry vegetable substance due to the extraneous supply of combined nitrogen being 8, 12, and even nearly 30-fold, according to the amount provided. Yet, with 19 experiments with Graminaceous plants, 6 with Leguminous ones, and some with plants of other descriptions, with such great variation in the amount and character of growth, and in the amount of combined nitrogen involved in the experiment in the several cases, in no instance have the results been such as to lead to the conclusion that there was an assimilation of free nitrogen.

The results of the whole enquiry may be briefly enumerated as follows:—

The yield of nitrogen in the vegetation over a given area of land, within a given time, especially in the case of Leguminous crops, is not satisfactorily explained by reference to the hitherto quantitatively determined periodical supplies of combined nitrogen.

Numerous experiments have been made by M. Boussingault, from which he concludes that free or uncombined nitrogen is not a direct source of the nitrogen of vegetation. M. G. Ville, on the other hand, concludes, from his results, that free nitrogen may be a source of a considerable proportion of the nitrogen of growing plants. The views, or explanations, of other experimenters, on this disputed point, are various and inconclusive.

It was found that the conditions of growth adopted in our own experiments on the question of the assimilation of free nitrogen, were consistent with the healthy development of various Graminaceous plants, but less so for that of the Leguminous plants experimented upon.

From the results of various investigations, as well as from other considerations, we think it may be concluded that, under the circumstances of our experiments, there would not be any supply to the plants of an unaccounted quantity of combined nitrogen, due either to the formation of oxygen-compounds of it under the influence of ozone, or nascent oxygen, or to that of ammonia under the influence of nascent hydrogen.

We have found that free nitrogen is given off in the decomposition of nitrogenous organic matter under certain circumstances. But, considering the circumstances of such evolution, and those to which the nitrogenous organic matter necessarily involved in experiments on the question of assimilation of free nitrogen is subjected, it may, we think, be concluded that there would be no loss of combined nitrogen from this cause in such experiments, excepting in certain cases when it might be pre-supposed.

Our experimental evidence, so far as it goes, does not favour the supposition that there would be any loss of combined nitrogen in the experiments on assimilation, due to the evolution of free nitrogen from the nitrogenous constituents of the plants during growth.

In numerous experiments with Graminaceous plants, grown both with and without a supply of combined nitrogen beyond that contained in the seed sown, in which there was great variation in the amount of combined nitrogen involved, and a wide range in the

conditions, character, and amount of growth, we have in no case found any evidence of an assimilation of free or uncombined nitrogen.

In our experiments with Leguminous plants, the growth was less satisfactory, and the range of conditions possibly favourable for the assimilation of free nitrogen was, therefore, more limited. But the results recorded with these plants, so far as they go, do not indicate any assimilation of free nitrogen. Since, however, in practice, Leguminous crops assimilate, from some source, so very much more nitrogen than Graminaceous ones, under ostensibly equal circumstances of supply of combined nitrogen, it is desirable that the evidence of further experiments with these plants, under conditions of more healthy growth, should be obtained.

Results obtained with some other plants are in the same sense as those obtained with Graminaceæ and Leguminosæ, in regard to the question of the assimilation of free nitrogen.

In view of the evidence of the non-assimilation of free nitrogen by plants under the wide range of circumstances provided in the experiments, it is desirable that the several actual or possible sources of *combined* nitrogen to plants should be more fully investigated, both qualitatively and quantitatively.

If it be established that the processes of vegetation do not bring free nitrogen into combination, it still remains not very obvious to what actions a large proportion of the existing combined nitrogen may be attributed.

XXI.—*Contributions to the History of the Tolyl Series.*

By Eugene Sell, of Bonn.

Preparation of Tolylamine.

During my residence in London in the course of last year, Dr. Hofmann received from Messrs. Collin and Coblenz, of Paris, a considerable quantity of the residues obtained in the manufacture of aniline (*queues d'aniline*, as they are called in the French factories). The examination of these residues has led Dr. Hofmann to the discovery of several new substances, an account of which has been already published in the Proceeding of the Royal Society.

In the portions of lower boiling point, the presence of tolylamine (toluidine) appeared probable, as the commercial benzol used in many factories for the preparation of tar-colours is almost invariably mixed with a quantity of the other hydrocarbons of the benzol series.

Some preliminary experiments confirmed the supposition, and at the same time supplied the means of procuring larger quantities of this interesting substance, so that its properties might be more minutely investigated.

The preparation of tolylamine from these residues was performed without much difficulty. A copper retort, provided with a thermometer and about half filled with the residues, was adapted to a long glass tube serving as a condenser. At first a very gentle heat is applied, as overheating is liable to produce a sudden ebullition and boiling over of the mass. When the water has all passed over, the receiver is changed, and the distillation continued until the temperature rises to 270°, by which time all the tolylamine will have passed over. The homogeneous clear brown liquid is introduced into a glass retort with a long neck, and redistilled with a thermometer. The bases passing between 180° and 230°, consisting almost entirely of aniline and tolylamine, with perhaps small traces of xylylamine, are converted into oxalates by the addition of a hot saturated solution of oxalic acid. By a few crystallisations, the oxalate of tolylamine, which is less soluble than the other oxalates, is easily separated; the purification has been carried sufficiently far, when a small quantity of the oxalate yields immediately, on addition of ammonia, a crystalline mass of tolylamine. The oxalate is then dissolved in hot water, and an excess of potassa or soda added, when the tolylamine separates as a brown oil, which floats on the aqueous solution, and solidifies on cooling.

The crystalline mass thus obtained is placed upon a filter, washed with cold water, until the washings are neutral to test paper, and dried by pressure between folds of bibulous paper. The dried mass is next distilled in a retort, when it almost entirely passes over between 198° and 200° C., solidifying in the receiver in snow-white crystals, which gradually assume a dark colour by exposure to the action of the air.

A considerable quantity of the base remains dissolved in the mother-liquor, from which it is deposited in small crystalline plates in the course of a few days.

With the tolylamine thus obtained, the following experiments were made :—

Tolyl-sulphamic Acid.

In preparing this acid, I followed the method employed by Messrs. Hofmann and Buckton, for the preparation of sulphanilic acid.*

Five grammes of finely divided tolylamine were submitted to the action of nine grammes of strong sulphuric acid very carefully added, drop by drop. The sulphate of tolylamine first formed by the reaction, which is violent at the commencement, is acted upon by the subsequent proportions of acid, and dissolved, a brown syrupy liquid being produced. The solution is next exposed to a moderate heat on a sand-bath, too high a temperature being carefully avoided, as it would cause the charring of the mixture.

When sulphurous acid gas begins to be evolved in considerable quantities, the liquid is removed from the sand-bath, slightly cooled, and poured into cold water. The coloured solution thus obtained is boiled for a few minutes with animal charcoal and filtered, and the limpid filtrate is evaporated, until it assumes a reddish yellow coloration. On cooling, the new acid is deposited in fine yellow needles, the formation of which is greatly accelerated by stirring the liquid with a glass rod. After two crystallisations from hot water, and the removal of the last traces of sulphuric acid by washing with cold water, the substance gave on analysis the following results :—

I.—0·3635 grm. of substance dried at 100°, and burnt with a mixture of chromate of lead and oxide of copper gave 0·5925 grm. of carbonic acid, and 0·1700 grm. of water.

II.—0·302 grm. of substance burnt with a mixture of carbonate of sodium and oxide of mercury gave 0·389 grm. of sulphate of barium.

The results of these analyses led to the formula—

$$C_7H_9N.SO_3 = \left.\begin{matrix} C_7H_7 \\ H_2 \end{matrix}\right\} N.SO_3.$$

* Chem. Soc. Qu. J. ix., 259.

	Theory.		Experiment. I.	Experiment. II.
C_7	84	44·92	44·43	—
H_9	9	4·81	5·17	—
N	14	7·48	—	—
S	32	17·11	—	17·54
O_3	48	25·68	—	—
	187	100·00		

The formation of the acid is therefore explained by the equation—

$$C_7H_9N + H_2SO_4 = C_7H_9N.SO_3 + H_2O.$$

The yellow needles are easily soluble in hot water, but sparingly soluble in cold. Potassa and ammonia dissolve them readily, forming the corresponding salts. The tolyl-sulphamate of silver gradually falls from a mixture of solutions of the neutral ammonium-salt and nitrate of silver. The white crystalline plates thus obtained, like the acid itself, are difficultly soluble in cold, but easily soluble in hot water; they assume a grey colour by the action of light.

0·520 grm. of the silver salt recrystallised from hot water gave on ignition 0·192 grm. of metallic silver, corresponding to a percentage of 36·92.

The formula—

$$C_7H_8AgN.SO_3 = \left.\begin{matrix} C_7H_7 \\ Ag \\ H \end{matrix}\right\} N.SO_3.$$

requires 36·73 per cent. of silver.

The other salts of tolyl-sulphamic acid are readily obtained by the action of the acid upon the corresponding carbonates. They are for the most part easily soluble in water. The barium salt crystallises by slow evaporation in small crystalline nodules.

The mother-liquors of the acid, after standing for some days, deposited rhombohedra of measurable dimensions, which exhibited the deportment of an acid. Probably they consisted of tolyl-disulphamic acid, corresponding to the disulphanilic acid of Messrs. Hofmann and Buckton; but the extremely small quantity obtained precluded the possibility of a more minute investigation.

Monotolylurea.

To a hot aqueous solution of sulphate of tolylamine a freshly prepared solution of cyanate of potassium is added. The transient formation of a milkiness on mixing the liquids is an indication of a reaction taking place, and, on cooling, white crystalline needles are deposited from the solution.

After two crystallisations from hot water, and drying at 100°, the crystals gave, on analysis, the following results:—

0·2435 grm. of substance burnt with oxide of copper, gave 0·572 grm. of carbonic acid and 0·148 grm. of water.

The formula—

$$C_8H_{10}N_2O = \left.\begin{matrix}(CO)'' \\ (C_7H_7) \\ H_3\end{matrix}\right\} N_2.$$

requires the following values, with which I contrast the results of the experiment—

	Theory.		Experiment.
C_8	96	64·00	64·06
H_{10}	10	6·66	6·73
N_2	28	18·66	—
O	16	10·68	—
	150	100·00	

The formation of the substance is therefore represented by the equation—

$$2KCNO + (C_7H_9N)_2.\ H_2SO_4 = 2C_8H_{10}N_2O + K_2SO_4.$$

The white needles are almost insoluble in cold, easily soluble in hot water; also in alcohol and ether. The solution has a sweet taste.

When submitted to the action of heat, they fuse at 158°, and decompose, evolving ammonia, and depositing in the neck of the retort crystals of ditolyl-urea, which will be described in one of the following paragraphs. That the substance in question really is ditolyl-urea, has been shown by the agreement of all its properties

with those of ditolyl-urea obtained by the process hereafter to be described, the very small quantity of the product not permitting a quantitative analysis.

The phenomena observed on submitting tolyl-urea to dry distillation, clearly indicate two different phases in the reaction.

Firstly, two equivalents of monotolyl-urea are decomposed into one equiv. of ditolyl-urea and one equiv. of ordinary urea—

$$2\left[\begin{matrix}(CO)''\\(C_7H_7)\\H_3\end{matrix}\right\}N_2\Bigg] = \begin{matrix}(CO)''\\(C_7H_7)_2\\H_2\end{matrix}\Big\}N_2 + \begin{matrix}(CO)''\\H_4\end{matrix}\Big\}N_2.$$

In the second stage, the urea is decomposed into ammonia and cyanuric acid.

It is necessary that I should in this place say a few words in justification of the name "monotolyl-urea" proposed for the compound above described, as the same name has been given by Dr. Noad to a substance obtained by a different process and possessing totally different chemical properties.

As is well-known, Dr. Hofmann prepared in 1846 a substance which he described under the name of aniline-urea, or monophenyl-urea, and which was the first compound urea obtained. The body in question may be prepared by different processes, and, amongst others, by the action of sulphate of aniline upon cyanate of potassium. This compound, however, failed to exhibit one of the properties of urea, which at that time was thought characteristic, namely, its capability of forming saline combinations by union with acids. A few years later, M. Chancel described a body obtained by the action of reducing agents upon nitrobenzamide, which was found to be isomeric with Hofmann's compound, and as it was shown to possess clearly defined basic properties, it was considered by the majority of chemists, and even by Gerhardt,* to be the true monophenyl-urea. While such were the opinions of chemists, Dr. Noad discovered his compound by a process analogous to the one employed by M. Chancel, viz., by the action of reducing agents upon nitrotolylamide, and consequently adopted the name of monotolyl-urea to represent its constitution. Since then, however, Dr. Hofmann, in a paper† communicated to the Royal Society, has drawn attention to these

* Gerhardt, Traité de Chimie Organique i, 427.

† "On Ureas and So-called Ureas." Proceedings of Royal Society, x, 601.

misconceptions, and has shown that the name of monophenyl-urea must be retained for the compound first obtained by himself. The arguments holding good in the phenyl-series are evidently applicable with equal force to the tolyl-series, and I may, therefore, refer to the above paper, in explanation of my reasons for applying the name of monotolyl-urea to the body described in the preceding paragraph.

Ditolyl-sulpho-urea.

This compound is prepared in the following manner. A concentrated alcoholic solution of tolylamine is mixed with about an equal volume of sulphide of carbon, and the mixture, contained in a flask provided with a vertical condensing arrangement, is digested at a temperature of 80° in a water bath. When the evolution of hydrosulphuric acid, which is at first very copious, has almost ceased, the excess of sulphide of carbon is removed by distillation. The alcoholic solution on cooling deposits yellowish crystals of ditolyl-sulpho-urea, which, after a few recrystallisations from hot alcohol, are sufficiently pure for analysis.

Dried at 100°, and submitted to combustion, they furnished the following results:—

I. 0·3895 grm. of substance, burnt with a mixture of chromate of lead and oxide of copper, gave 1·003 grm. of carbonic acid, and 0·2215 grm. of water.

II. 0·5385 grm. of substance, burnt with a mixture of carbonate of sodium and oxide of mercury, gave 0·4980 grm. of sulphate of barium.

These numbers lead to the formula—

$$C_{15}H_{16}N_2S = \left.\begin{matrix}(CS)'' \\ (C_7H_7)_2 \\ H_2\end{matrix}\right\} N_2.$$

	Theory.		Experiment.	
			I.	II.
C_{15}	180	70·31	70·22	—
H_{16}	16	6·25	6·31	—
N_2	28	10·94	—	—
S	32	12·50	—	12·68
	256	100·00		

The formation of the compound is represented by the equation—

$$2(C_7H_9N) + CS_2 = C_{15}H_{16}N_2S + H_2S.$$

Ditolyl-sulpho-urea or ditolyl-sulpho-carbamide—for this is the more appropriate name for the new compound—is insoluble in water and cold alcohol, soluble, though with some difficulty, in hot alcohol. It recrystallises in well formed prisms of considerable size, melting at 164°, and subliming without decomposition.

Like the corresponding term of the phenyl-series, this substance is characterised by an extraordinarily bitter taste; its vapours have a pungent odour, distantly resembling that of anise-seed oil.

As this substance is easily prepared in large quantities, it affords the most convenient starting point for the preparation of

Ditolylurea.

For this purpose, freshly precipitated oxide of mercury is gradually added by small portions to a hot alcoholic solution of ditolyl-sulphocarbonyl-diamide, until the oxide of mercury no longer becomes black by conversion into sulphide.

The solution separated from the mercury by hot filtration, deposits the ditolylurea on cooling in the shape of white crystals, which, when purified by repeated recrystallisations from hot alcohol were submitted to analysis.

0·328 grm. of the substance dried at 100°, when burnt with oxide of copper, gave 0·902 grm. of carbonic acid, and 0·203 grm. of water.

These numbers nearly coincide with the theoretical value of the formula—

$$C_{15}H_{16}N_2O = \left.\begin{matrix}(CO)'' \\ (C_7H_7)_2 \\ H_2\end{matrix}\right\} N_2.$$

	Theory.		Experiment.
C_{15}	180	75·00	75·00
H_{16}	16	6·66	6·87
N_2	28	11·68	—
O	16	6·66	—
	240	100·00	

Ditolyl-urea is insoluble in water, slightly soluble in cold and very soluble in hot alcohol; by the action of concentrated sulphuric acid, it is transformed into tolyl-sulphamic acid. The solution, when neutralised with carbonate of barium, and filtered from the sulphate of barium, yields by slow evaporation crystals of tolyl-sulphamate of barium.

Another process for obtaining ditolyl-urea is, as already mentioned, the dry distillation of monotolyl-urea, by which ditolyl-urea is formed, simultaneously with the products of the decomposition of ordinary urea.

Tolyl-ethyl-urea.

Finely divided tolylamine is submitted in a convenient apparatus to the action of cyanate of ethyl, which is added, drop by drop, until it is no longer absorbed by the tolylamine. The action of the substances upon one another is extremely violent, the product being a yellow crystalline mass, which is most conveniently purified by recrystallisation from a hot mixture of equal parts of alcohol and water.

In a state of purity, the crystals are perfectly white; their analysis has furnished the following results:—

0·275 grm. of substance dried at 100°, and burnt with oxide of copper, yielded 0·677 grm. of carbonic acid and 0·197 grm. of water.

This analysis leads to the formula—

$$C_{10}H_{14}N_2O = \left.\begin{matrix}(CO)'' \\ C_2H_5 \\ C_7H_7 \\ H_2\end{matrix}\right\} N_2.$$

	Theory.		Experiment.
C_{10}	120	67·41	67·27
H_{14}	14	7·86	7·92
N_2	28	15·73	—
O	16	9·00	—
	178	100·00	

Tolyl-ethyl-urea is simply produced by the direct union of the two constituents—

$$C_7H_9N + C_2H_5.CNO = C_{10}H_{14}N_2O.$$

Its deportment and properties are very similar to those of the phenyl-ethyl-urea prepared and described by Wurtz.

Tolyl-succinyl-amide and Ditolyl-succinyl-diamide.

These two substances are obtained in the following manner:—

About equal parts by weight of pulverised succinic acid and tolylamine are well mixed, and heated for some time on a sand-bath in a glass vessel. The succinate of tolylamine first obtained by the fusion is decomposed by the further action of heat, aqueous vapours being copiously evolved. The mass thus produced, solidifies on cooling into a crystalline cake which, by treatment with boiling water, is separated into the two compounds, *tolyl-succinyl-amide* and *ditolyl-succinyl-diamide*.

The hot aqueous solution is filtered, and deposits, on cooling, colourless crystals of tolyl-succinyl-amide, which are easily purified by repeated crystallisation from hot water.

Dried at 100° and burnt with oxide of copper, 0·326 grm. of the substance gave 0·834 grm. of carbonic acid and 0·175 grm. of water.

These numbers lead to the formula—

$$C_{11}H_{11}NO_2 = \left.\begin{matrix} C_7H_7 \\ (C_4H_4O_2)'' \end{matrix}\right\} N.$$

	Theory.		Experiment.
C_{11}	132	69·84	69·75
H_{11}	11	5·82	5·96
N	14	7·40	—
O_2	32	16·94	—
	189	100·00	

The substance is formed by the expulsion of two equivalents of water from the primary succinate of tolylamine—

$$C_7H_9N.C_4H_6O_4 - 2H_2O = C_{11}H_{11}NO_2.$$

Tolyl-succinylamide is insoluble in cold soluble in hot water, also in alcohol and ether. It may be volatilised without decomposition.

The residue left after treatment of the melted product with boiling water, appears in the form of silver-grey scales. It is purified for analysis by recrystallisation from hot alcohol.

On combustion with oxide of copper, 0·243 grm. of substance dried at 100°, gave 0·643 grm. of carbonic acid and 0·154 grm. of water.

The percentages corresponding to these experimental numbers approximate, though by no means so closely as could be desired, to the theoretical values of the formula—

$$C_{18}H_{20}N_2O_2 = \left.\begin{matrix}(C_7H_7)_2\\(C_4H_4O_2)''\\H_2\end{matrix}\right\}N_2.$$

	Theory.		Experiment.
C_{18}	216	72·93	72·02
H_{20}	20	6·75	7·03
N_2	28	9·45	—
O_2	32	10·87	—
	296	100·00	

Ditolyl-succinyl-diamide is formed by the expulsion of two equivalents of water from the secondary succinate of tolylamine—

$$(C_7H_9N)_2 . C_4H_6O_4 - 2H_2O = C_{18}H_{20}N_2O_2.$$

Cyan-tolylamine.

In conclusion I may be permitted to add a few remarks on cyan-tolylamine. This substance was first prepared and described by Dr. Hofmann,* who did not, however, analyse it, since its ana-

* Chem. Soc. Qu. J. i, 160.

logy with cyan-phenylamine placed its composition beyond a doubt. I append an analysis which entirely confirms the formula given by Dr. Hofmann.

0·2205 grm. of cyantolylamine, dried at 100°, and burnt with oxide of copper, gave 0·5815 grm. of carbonic acid gas, and 0·1390 grm. of water.

The formula—

$$C_8H_9N_2 = \left.\begin{matrix}(CN)(C_7H_7)\\H_2\end{matrix}\right\}N.$$

requires the following values—

	Theory.		Experiment.
C_8	96	72·18	71·96
H_9	9	6·76	6·97
N_2	28	21·06	—
	133	100·00	

In order to study the deportment of cyan-tolylamine under the influence of boiling acids, I dissolved a quantity in dilute hydrocloric acid, expecting to obtain products of decomposition analogous to those described by Dr. Hofmann,* in his investigation of the corresponding phenyl-compound.

At first my expectations were rather disappointed, for I found that the crystals obtained by evaporation were easily dissolved by cold water. A more minute examination proved them to consist entirely of hydrochlorate of tolylamine, which had been reproduced by an accidental excess of the acid being present in the solution. The experiment repeated in a similar manner with cyan-phenylamine yielded only hydrochlorate of phenylamine.

A perfectly different result was obtained when a neutral hydrochloric solution of cyan-tolylamine was submitted to ebullition. The liquid thus obtained deposited on evaporation white crystals which, by treatment with cold and hot water, were separated into three different portions. Unfortunately, the nearly exhausted supply of tolylamine at my disposal, prevented my making the experiment upon a sufficiently large scale, and the quantities of the several substances ultimately separated were not sufficiently large to

* Ann. Ch. Pharm., lxxiii, 180.

admit of analysis. The qualitative phenomena, however, which I have observed, leave no doubt that the products of decomposition of cyan-tolylamine under these circumstances are perfectly analogous to those of cyan-phenylamine, and that, in addition to the chlorides of ammonium and tolylammonium, this decomposition produces the following substances—

Normal Oxamide.

$$C_2H_4N_2O_2 = \left.\begin{matrix}(C_2O_2)'' \\ H_2 \\ H_2\end{matrix}\right\}N_2.$$

Monotolyl-oxamide.

$$C_9H_{10}N_2O_2 = \left.\begin{matrix}(C_2O_2)'' \\ (C_7H_7) \\ H_3\end{matrix}\right\}N_2.$$

Ditolyl-oxamide.

$$C_{16}H_{16}N_2O_2 = \left.\begin{matrix}(C_2O_2)'' \\ (C_7H_7)_2 \\ H_2\end{matrix}\right\}N_2.$$

I cannot conclude this paper without expressing my best thanks to Mr. E. Thomas for his kindness in placing at my disposal a large quantity of toluol, from which a further quantity of tolylamine was prepared when the supplies from the "*queues d'aniline*" had been exhausted.

The above experiments were carried out in Dr. Hofmann's laboratory.

XXII.—*Note on the Chloromaleic Acid obtained from Tartaric Acid.*

By W. H. Perkin.

Some time since, Mr. Duppa and myself gave an account of the action of pentachloride of phosphorous on tartaric acid. We then showed that these two bodies react on each other, producing hydrochloric acid, oxychloride of phosphorus, and an oily chloride, which is rapidly converted into an acid when left in contact with

water. In composition this acid represents either maleic or fumaric acid, in which one equivalent of hydrogen is replaced by chlorine; we therefore named it *chloromaleic acid*, as its solubility coincided more with that of maleic acid than with that of fumaric acid; but having some doubts as to whether this acid really bore any relation to maleic acid, I was induced to try whether I could replace its chlorine by hydrogen, and thereby produce maleic acid. I proceeded in the following manner:—

A quantity of a solution of chloromaleate of potassium was subjected to the influence of sodium-amalgam for two or three hours. It was then decanted from the mercury, acidulated with hydrochloric acid, and evaporated to dryness over a water-bath; the dry residue was then digested with ether two or three times. The resulting ethereal solution, on being evaporated, deposited a white crystalline acid having the peculiar taste of succinic acid, and when heated, emitting the suffocating vapour so characteristic of that acid. Its salts also produced, with sesquichloride of iron and other re-agents, all the usual re-actions of succinic acid.

Two combustions of this product, after having been twice crystallised from water, gave the following numbers:—

I.	·28125	of substance gave
	·41925	of carbonic acid, and
	·136	of water.
II.	·28625	of substance gave
	·427	of carbonic acid, and
	·1335	of water.

Per centage composition—

	I.	II.
Carbon.....	40·65	40·64
Hydrogen....	5·3	5·18

The formula of succinic acid requires C 40·67 and H 5·08. Therefore, this acid is undoubtedly succinic acid.

Although this result is not exactly what I hoped to obtain, yet it is what we might have expected. The researches of Kekulé have shown that maleic acid readily combines with two equivalents of hydrogen and produces succinic acid. Therefore, the moment chloromaleic acid becomes changed, the resulting maleic acid is supplied with more nascent hydrogen, and is thereby converted into succinic acid.

The change of the acid under consideration into succinic acid by the action of nascent hydrogen, proves then, I *think*, that it really is what it was first named, viz., *chloromaleic acid*. The reaction above-described may be written thus :—

$$\underset{\text{Chloromaleic acid.}}{C_4(H_3Cl)O_4} + HH = \underset{\text{Maleic acid.}}{C_4H_4O_4} + HCl.$$

$$C_4H_4O_4 + HH = \underset{\text{Succinic acid.}}{C_4H_6O_4}.$$

It is interesting to observe that from succinic acid we can prepare paratartaric acid, and that from ordinary tartaric acid we can obtain succinic acid.

XXIII.—*On Pickeringite occurring in Slate in Nova Scotia, and on the Class of Salts to which it belongs.*

By Professor How, D.C.L., University of King's College, Windsor, Nova Scotia.

Pickeringite does not appear to be a common mineral; it is not mentioned by Greg and Lettsom among the minerals of Great Britain, and only one analysis of it is recorded by Nicol and by Dana, that of a specimen from Iquique, in Peru, by Dr. Hayes. The subject of the present paper was found on the bank of the Meander, a small river in Newport, Hants Co., N.S. It occurs as an efflorescence on slate sheltered from the rain by overhanging ledges of the same rock; the cliff upon which I saw it was about 60 feet high, and nearly perpendicular. Some of the rock was of a rusty colour, compact and tolerably hard, and showed little or no pickeringite; another kind was bluish-black, and of such texture as to crumble easily between the fingers; on this the mineral was conspicuous, seeming to be disseminated through it, and was besides often met with on the edges in rather dense masses of somewhat mammillary form, about half an inch thick, exposing a surface of some square inch or two in extent; these were for the most part amorphous externally and tolerably homogeneous, but there were other lighter or more open masses, showing

a distinct silky, crystalline, plumose structure, and enclosing abundance of fragments of slate, which were generally very thin, and of various sizes, being often quite minute. These masses were sometimes half the size of a man's fist. Occasionally the slate was, as it were, wedged apart into sheets at or near the edges, and compact inwards. These conditions of occurrence point to a formation of the mineral from the rock under atmospheric influence.

The mineral was snow-white and also yellowish, opaque, sometimes in powdery lumps, apparently amorphous, often crystallised in short silky needles. It was soft (hardness = 1), soluble in water, with the taste of alum. In the mattrass, it gave water and swelled up considerably, leaving a bulky white residue which gave the alumina reaction with nitrate of cobalt. After preliminary qualitative analysis, the following results were obtained on determining the quantities of the constituents in the air-dried mineral. The nickel and cobalt were separated by means of nitrate of potassa. The sulphuric acid in I. was calculated from the concordant results of II. and III., the water was determined by gradual heating below redness.

	I.	II.	III.	IV.
Oxide of copper.....	0·02			
Alumina.....	10·64	11·19		
Protoxide of iron*....	0·13			
Magnesia	4·79			
Oxide of cobalt.....	0·06			
Oxide of nickel.....	0·14			
Oxide of manganese..	0·45			
Potassa	0·23			
Water.....	46·06	46·16	46·07	45·43
Sulphuric acid	36·33	36·36	36·59	
Slate	0·72	0·40	0·33	0·48
	99·57			

A comparison of these results with those obtained by Dr. Hayes in the analyses of pickeringite, from Iquique in

* Sulphocyanide of potassium gave no red colour in solution of the mineral.

Peru, shows that the subject of my paper is really the species by found Dr. Hayes.*

Al_2O_3	MgO	FeO + MnO	CaO	HCl	SO_3	HO	
12·13	4·682	0·430	1·26	0·604	36·322	45·45	=99·744

On examining my mineral and a specimen of that from Iquique, received some few years ago from Professor Cooke, of Harvard College, under the microscope, I found them both to exhibit oblique prisms, the latter affording much the larger crystals.

The determinations of water in my analyses were made at intervals between September 29th (3 days after date of collecting) and December 23rd following, the mineral being kept in a room subject to changes of temperature; from the agreement of these determinations among themselves, and with the result of Dr. Hayes, it is evident that the composition of the mineral in this respect is perfectly constant. This being the case, I wish to point out that the name "pickeringite" is preferable to that of magnesia-alum for the mineral, because it is not really an alum, inasmuch as it has neither of the well-known characteristics of alums, viz., the 24 atoms of water in the equivalent of the salt, and the octahedral crystal form. Certain salts are thus adverted to by Professor Miller.† "Besides the true alums, a number of double salts of alumina may be formed with the sulphates of the oxides isomorphous with magnesia, which crystallise in fine silky needles. A native sulphate of alumina and manganese was found by Kane and Apjohn, to contain 25 equivalents of water, for which Graham proposes the formula $MnO.SO_3.HO + Al_2O_3.3SO_3 + 24aq$, representing a compound of the sulphate of manganese with its equivalent of constitutional water, in combination with tersulphate of alumina. A similar salt of iron has been met with in the native state."

On reviewing the analyses of alums given in Dana, I am led to the conclusion that pickeringite belongs to a class of salts, of which several exist native, distinguished from true alums by having the formula of these salts minus two equivalents of water, and by crystallising in prismatic forms. Moreover, bearing in mind the ease with which sulphuric acid is driven off from such salts at a red heat, I think it probable that the salt of Apjohn

* Dana's Mineralogy, 4th ed., p. 382. Nicol's Mineralogy, p. 323.

† Elements of Chemistry. II. 528

and Kane, mentioned by Miller, really belongs to this class, but, from losing sulphuric acid on ignition, such acid being considered as water, has not had its real composition assigned to it. The salt in question is no doubt that of which an analysis by Apjohn is given in Dana,* under the head of manganesian alum; the results are these—

Al_2O_3 10·65; Mn_2O_3 7·33†; SO_3 32·79; HO 48·15; $MgO{\cdot}SO_3$ 1·08 = 100,

a comparison of which, with the percentage calculated from the two following formulæ, shews that such an error as the one adverted to, would at once lead to a wrong formula; it would only sensibly affect the water and acid—

MnO	=	35·57	7·53		
Al_2O_3	=	51·40	10·88		
$4SO_3$	=	160·00	33·90		
25HO	=	225·00	47·69		
		471·97	100·00		
MnO	=	35·57	7·99		
Al_2O_3	=	51·40	11·51		
$4SO_3$	=	160·00	35·96		
22HO	=	198·00	44·54		
		444·97	100·00		

In order to ascertain the effect of a red heat on such salts, I subjected some pickeringite to this temperature; it lost 60 instead of 46 per cent., and on igniting the residue again, a blue test-paper was strongly reddened, when held for an instant in the crucible. If the heat rose too high, therefore, in a solitary experiment (and only one analysis of the salt is given) the results of which were made the basis of calculation, error would certainly ensue in working out a formula.

An argument in favour of the formula I assign to apjohnite is found in comparing the results of the analysis of a manganomanganesian alum by Stromeyer,‡, with the percentages of the formula following :—

* Dana's Mineralogy, 4th ed., p. 383.
† Nicol, Mineralogy, p. 323, gives this as MnO.
‡ Dana, p. 382.

			Stromeyer.
$\frac{2}{3}MgO$	=	13·33	3·06	3·69
$\frac{1}{3}MnO$	=	11·85	2·73	2·167
Al_2O_3	=	51·40	11·83	11·515
$4SO_3$	=	160·00	36·82	36·770
22HO	=	198·00	45·56	45·739
				KCl 0·205
		434·58	100·00	100·086

No crystalline form is mentioned by Dana, but Nicol* says, the salt is silky when newly exposed. On the view taken by Graham, from the analysis of Kane and Apjohn, their salt would be quite anomalous, but in that I would adopt, Stromeyer's salt would be apjohnite, in which the manganese is greatly ($\frac{2}{3}$) replaced by magnesia, a compound coming very near pickeringite, which resembles them both apparently in forming fibrous crystals.

As regards pickeringite, the percentages belonging to the formula of a true alum and to that of the same minus two atoms of water, are here placed side by side—

MgO	=	20·0	4·47	MgO	=	20·0	4·66
Al_2O_3	=	51·4	11·49	Al_2O_3	=	51·4	11·97
$4SO_3$	=	160·0	35·76	$4SO_3$	=	160·0	37·26
24HO	=	216·0	48·28	22HO	=	198·0	46·11
		447·4	100·00			429·4	100·00

and a comparison between them, and the results of analysis given in the former part of this paper, shows clearly, I think, that the essential difference adverted to really obtains; it becomes more obvious, perhaps, after deduction of the slate, when the essential ingredients stand thus:—

Analysis I. (p. 201)

MgO	=	4·84
Al_2O_3	=	10·76
SO_3	=	36·74
HO	=	46·59
		98·93

* Mineralogy, p. 322.

The "Hversalt," of Forchammer* is evidently an allied salt; we may regard it as pickeringite in which the magnesia is half replaced by protoxide of iron, part of the alumina being at the same time replaced by peroxide of iron, as seen in the following comparison:—

				Forchammer.
$\frac{1}{2}MgO$	=	10·	2·29	2·19
$\frac{1}{2}FeO$	=	18·	4·11	4·57
Al_2O_3	=	51·4	11·75	11·22 + Fe_2O_3 1·23
$4SO_3$	=	160·0	36·58	35·16
22HO	=	198·0	45·27	45·63
		437·4	100·00	100·00

Lastly, we have the ferrous salt belonging to this class in the mineral "Iron Alum, Federalaun, Haarsalz in part" which crystallizes in fibrous silky crystals: the analyses given are—

	Al_2O_3	FeO	SO_3	MgO	HO	KO			
1.	8·8	12·00	34·400	0·8	44·00		=	100·	Berthier.
2.	10·914	9·367	36·025	0·235	43·025	0·434	=	100·	Rammelsberg.
3.	10·617	8·150	33·812		41·611	SiO_3 3·34	Fe_2O_3	1·05 = 99·58	B. Silliman, jun.

On comparing these numbers with the percentages belonging to the following formula—

FeO	36·0	8·08
Al_2O_3	51·4	11·54
$4SO_3$	160·0	35·93
22HO	198·0	44·45
	445·4	100·00

it becomes apparent, that taking them together and allowing for replacements, the formula expresses the composition of the normal iron-salt to which the minerals analysed are referable. This salt is most probably the "salt of iron," alluded to by Professor Miller,

* Dana, Mineralogy, p. 383.

"as similar" to the manganese-salt of Apjohn and Kane discussed in this paper.

We have then, I think it must be allowed, in the minerals brought under notice, *not alums*, but a well-marked group of salts, which have the general formula—

$$RO.SO_3 + R_2O_3.SO_3 + 22aq.,$$

and crystallize in prismatic forms, generally in silky needles, made up, judging from those of pickeringite, of oblique prisms.

An interesting feature in the pickeringite described in this paper, is the presence of small quantities of nickel and cobalt. Finding these metals in the mineral, I looked for them in the slate. I took some of the most solid, which showed no pickeringite, and fused about 40 grains with carbonated alkali, but found neither of the metals. I also took some of the dark-coloured friable slate, and, after washing out all the pickeringite, fused about 40 grains with carbonated alkali, but found neither nickel nor cobalt. The slate showed no crystals to the naked eye, but it gave sulphurous acid on being roasted, and contained considerable quantities of iron. The nickel and cobalt were, therefore, most probably present in pyrites, in which form of combination, Hunt found a thousandth of nickel in magnesite* from Bolton, Canada. I ought to have detected these metals had they been present as part of the slate, in combination with silica, a form in which nickel occurs frequently, in small amount, in the magnesian rocks of the Quebec group,† being seldom or never absent from the serpentines, steatites, diallages, and actinolites of the series, but rarely forming more than two or three thousandths. It would be interesting to prove whether this is the case with the other minerals from the Nova Scotia rocks of the Silurian system, to which the slate affording the pickeringite now noticed, probably belongs.

* Report on Geology of Canada, 1863, p. 507. † Loc. cit.

XXIV.—*On some Derivatives of Naphthylamine.*

By W. H. Perkin and A. H. Church.

In the Quarterly Journal of the Chemical Society for 1856,* we gave an account of some new bodies, which, from their mode of formation, and the results of their analysis, we were induced to view as compounds in which hydrogen had been replaced by binoxide of nitrogen. One of these bodies was produced by the action of nascent hydrogen on dinitrobenzole; the other was obtained by treating a salt of naphthylamine with nitrite of potassium. It is this last-named substance which we have subjected to a more careful scrutiny, and the results of our investigation we place before the Society in the present communication, hoping, as opportunity offers, to submit nitrosophenyline also to a fresh examination.

In our previous paper, we stated that when nitrite of potassium is added to a salt of naphthylamine, a reddish-brown precipitate is immediately produced, which, when washed and dried, dissolves in alcohol, forming an orange-red solution. This solution, evaporated to dryness on the water-bath, left a dark crystalline residue, having a green metallic reflexion. From specimens of a product prepared in this manner, we obtained analytical results corresponding with the formula :—

$$C_{10}H_8N_2O.$$

These results naturally led us to explain the formation of the body thus :—

$$C_{10}H_9N.HCl + KNO_2 = C_{10}[H_8(NO)]N + H_2O + KCl.$$

But the subsequent discovery of ninaphthylamine, which has exactly the same formula as that which we assigned to this body, induced us, as we had large quantities of naphthylamine at our disposal, to re-investigate this interesting substance; and the results we now record show that the product previously examined by us, which yielded numbers so strangely according with the

* Vol. ix, p. 1.

formula given above, was far from being a definite body, but was, in fact, a mixture of two or more substances. Unacquainted with any test for the purity of our product, and adopting a mode of preparation which was essentially faulty, it is not to be wondered at that we arrived at conclusions which have now to be revised. No substances have given rise to such conflicting formulæ and opinions as have colouring matters, both natural and artificial, and the very early appearance of the so-called nitroso-naphthyline in the history of coal-tar colours, is an additional reason why an immediate discovery of its relations was not made.

We find that when a solution of nitrite of potassium is added to a solution of a salt of naphthylamine, a precipitate is always formed; but this re-action is by no means a definite one, as the precipitate is seldom possessed of the same characteristics. Sometimes it is brownish red, sometimes dark brown, and sometimes it appears to be a mixture of red and brown particles.

If a quantity of the dark brown precipitate above-named be boiled in alcohol, it dissolves, but does not appear to have any tendency to crystallise: if this solution be evaporated to half its bulk, it will gradually deposit a few short, dark-coloured crystals, having jagged edges. But if a bright brownish red precipitate has been obtained, when it is boiled with alcohol, it will deposit, on cooling, a large quantity of beautiful orange-red needles, having a green metallic reflexion. The dark-coloured crystals obtained from a brown precipitate gradually assume this character, if re-crystallised six or seven times from boiling alcohol. Specimens obtained from precipitates of various characters, and often re-crystallised from boiling alcohol, when dried at 100° C, gave, on analysis, the following numbers:—

Carbon and Hydrogen Determinations.

I.	·2433	grm.	substance,	gave	·72175	grm.	CO_2	and	·118	grm. H_2O
II.	·20875	„	„	„	·61625	„	„	„	·1035	„ „
III.	·2535	„	„	„	·753	„	„	„	·129	„ „
IV.	·3015	„	„	„	·8925	„	„	„	·14825	„ „
V.	·3015	„	„	„	·8935	„	„	„	·1455	„ „
VI.	·387	„	„	„	1·145	„	„	„	·185	„ „
VII.	·207	„	„	„	·613	„	„	„	·1037	„ „
VIII.	·2641	„	„	„	·7847	„	„	„	·1248	„ „

Direct Nitrogen Determinations.

IX. ·323 grm. substance gave 39·0 cc. N. at 15° C., and 754·3 mm. Bar.

$$V' = \frac{39{\cdot}0 \text{ cc. } (754{\cdot}3 \text{ mm.} - 12{\cdot}7 \text{ mm.})}{801{\cdot}8 \text{ mm.}} = 36{\cdot}07 \text{ cc. at } 0° \text{ C., and } 760 \text{ mm. Bar.}$$

36·07 cc. × ·0012577 grm. = ·045365 grm. N.

X. ·304 grm. substance gave 37°0 cc. N. at 15° C., and 759·4 mm. Bar.

$$V' = \frac{37{\cdot}0 \text{ cc. } (759{\cdot}4 \text{ mm.} - 12{\cdot}7 \text{ mm.})}{801{\cdot}8 \text{ mm.}} = 34{\cdot}45 \text{ cc. at } 0° \text{ C. and } 760° \text{ mm. Bar.}$$

34·45 cc. × ·0012577 grm. = ·04325 grm. N.

The foregoing analytical results correspond to the percentages embodied in the table below:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Carbon	80·81	80·51	81·0	80·73	80·802	80·69	80·76	81·03	—	—
Hydrogen	5·38	5·5	5·63	5·4	5·36	5·31	5·5	5·25	—	—
Nitrogen	—	—	—	—	—	—	—	—	14·02	14·22

Excluding the hydrogen in analysis III, the mean of the foregoing experiments is given below in comparison with the theoretical percentages of carbon, hydrogen, and nitrogen, demanded by the formula which analysis has indicated:—

	Experiment. (Mean).	Theory. ($C_{20}H_{15}N_3$).
Carbon	80·784	80·81
Hydrogen	5·39	5·05
Nitrogen	14·12	14·14
	100·294	100·00

The preceding results were obtained in the analysis of various preparations. Some of the specimens had been extracted from evidently impure precipitates; some were of a difficultly crystallisable product, which, at one time, we were inclined to regard as a modification of the substance under examination; while others had been obtained by an improved process shortly to be described. From several combustions of this last-named preparation, we select the two that follow; the substance had been re-crystallised many times from absolute alcohol:—

XI. ·307 grm. sub. gave ·9105 grm. CO_2 and ·145 grm. H_2O
XII. ·28 „ „ „ ·8325 „ „ „ ·1335 „ „

These results correspond to the following percentages:—

	XI.	XII.	Theory ($C_{20}H_{15}N_3$).
Carbon	80·88	81·05	80·81
Hydrogen	5·24	5·28	5·05
Nitrogen	—	—	14·14
			100·00

These results evidently designate $C_{20}H_{15}N_3$ as the formula for the substance, which we propose to name "azodinaphthyldiamine," in accordance with its apparent constitution—2 eqs. of naphthylamine united by the substitution of 1 eq. of nitrogen for 3 eqs. of hydrogen:—

$$\left.\begin{matrix} C_{10}H_7 \\ N''' \\ H \\ C_{10}H_7 \end{matrix}\right\}N = C_{20}H_{15}N_3.$$

It is clear, therefore, that the fault of the older mode of preparing azodinaphthyldiamine lay in the employment of twice the necessary quantity of nitrous acid. To obviate this defect, we now take to 2 eqs. of hydrochlorate of naphthylamine, 1 eq. of nitrite of potassium and 1 eq. of hydrate of potassium; 1 eq. of naphthylamine is thus set free, and the re-action takes place as follows:—

$$2(C_{10}H_9N.HCl) + KHO + KNO_2 = C_{20}H_{15}N_3 + 2KCl + 3H_2O.$$

This new method of preparation yields a remarkably beautiful and pure product, which may be obtained in fine crystals by one or two crystallisations from boiling alcohol, in which, however, it is but slightly soluble.

We have but few additions to make to the description which we formerly gave of the chief chemical and physical characteristics of azodinaphthyldiamine. In order that the present paper may be more complete, we will, however, recapitulate these points here.

Azodinaphthyldiamine is insoluble in cold water; to water at 100° it imparts a yellow tint. It is soluble in alcohol, ether, and benzole, but not to a large extent; these liquids, however, when raised to the boiling-point, are capable of dissolving a considerably greater proportion. With most acids azodinaphthyldiamine in solution becomes of a rich and deep violet tint, the original orange-red colour being restored by alkalies and even by water. With oil of vitriol the dry crystals produce a dull green colour, which, by the addition of a trace of water, becomes intensely blue; if more water be present, the usual violet shade is obtained. With strong nitric acid azodinaphthyldiamine strikes a brown tint, immediately dissolving without the evolution of any gas. The colour afterwards becomes brownish red; if water be added to this solution, a brown precipitate is obtained. Long boiling with caustic

potash reproduces from azodinaphthyldiamine a portion of naphthylamine.

Azodinaphthyldiamine may be heated considerably without decomposition. At 135° C. it fuses to a blood-red liquid having a green metallic lustre. A drop of its alcoholic solution allowed to evaporate on a glass slide affords a beautiful object when examined microscopically by incident light; the crystals are generally arranged in stellate groups.

Action of Acids on Azodinaphthyldiamine.

The violet solutions produced by the addition of acids to azodinaphthyldiamine dissolved in spirit, contain saline compounds in which part at least of the acid is retained somewhat feebly.

With hydrochloric acid, azodinaphthyldiamine appears to unite in several proportions. When to a cold saturated solution of this base, a small quantity of aqueous hydrochloric acid is added, brilliant golden-brown flat prisms gradually separate. Washed with alcohol, acidulated with hydrochloric acid, and then dried over sulphuric acid in presence of potash, they gave on analysis the following numbers:—

I.	·616	grm. of substance	gave	·068	grm. of chloride of silver
II.	1·05	„ „		·117	„ „
III.	1·37	„ „		·1505	„ „

These results correspond to the following percentages of hydrochloric acid:—

I.	II.	III.
2·81	2·83	2·86

and accord with the proportion of hydrochloric acid contained in a compound of 4 eqs. of base and 1 eq. of acid—

$$(C_{20}H_{15}N_3)_4.HCl.$$

This formula requires 2·97 per cent. of hydrochloric acid.

If to a hot alcoholic solution of azodinaphthyldiamine about 1-10th of its volume of strong aqueous hydrochloric acid diluted with an equal bulk of alcohol be added, dark purplish-red crystals

are deposited on standing. These crystals, dried over sulphuric acid in presence of potash, gave the following results :—

I. ·375 grm. substance gave ·1587 grm. AgCl.
II. ·291 „ „ „ ·1225 „ „
III. ·3405 „ „ „ ·139 „ „

These results correspond to the following percentages of hydrochloric acid—

I.	II.	III.
10·77	10·68	10·39

and accord with the proportion of hydrochloric acid contained in a compound of 1 eq. of base and 1 eq. of acid—

$$C_{20}H_{15}N_3.HCl.$$

This formula requires 10·95 per cent. of hydrochloric acid.

If to a hot alcoholic solution of azodinaphthyldiamine, a very great excess of concentrated aqueous hydrochloric acid be added, the mixture becomes nearly solid from the separation of bulky crystals of a yellow-brown colour by transmitted light, and having a green lustre when wet. Drained from the mother-liquor, washed with strong aqueous hydrochloric acid, and dried over sulphuric acid in presence of potash, till constant in weight, these crystals were submitted to analysis with the following results :—

I. ·433 grm. gave ·301 grm. AgCl
II. ·2615 „ „ ·2095 „ „

These results correspond to the following percentages of hydrochloric acid—

I.	II.
19·43	19·49

and accord well with the proportion of hydrochloric acid contained in a compound of 1 eq. of base and 2 eqs. of acid—

$$C_{20}H_{15}N_3.2HCl.$$

This formula requires 19·78 per cent. of hydrochloric acid.

The three hydrochlorates above described appear to be very definite salts. The first described, containing 4 eqs. of base to 1 eq. of acid, dissolves in alcohol with an orange-red colour hardly

to be distinguished from that of the pure base under the same circumstances. The second hydrochlorate, $C_{20}H_{15}N_3.HCl$, gives a crimson solution; while the third salt, in which the biatomic character of azodinaphthyldiamine is shown, dissolves in alcohol with the magnificent violet colour characteristic of a solution of that base to which acid has been added. When attempts are made to recrystallise salts 2 and 3 from alcohol, they are partially resolved into salt 1, which appears scattered among the darker salts in the form of stellate groups of golden-brown crystals. Washing with cold water, unless long continued, does not decompose the hydrochlorates. If properly prepared and dried, they produce no red coloration when placed on blue litmus paper and then moistened with water. But hot water, and alkaline liquids remove part of the acid. In the hydrochloric acid determinations, the weighed salt was first completely dissolved in alcohol, and then alcoholic solution of soda was added to the liquid. Afterwards, on the addition of water, the base, which separates completely as a scarlet or crimson precipitate, is removed by filtration, and the chlorine determined in the usual way, in the filtrate. The same process was adopted in analysing the sulphate next described.

Attempts to obtain a satisfactory platinum-salt, have not as yet been attended with success.

When sulphuric acid is added to a cold saturated solution of azodinaphthyldiamine, the violet solution deposits, on standing, a quantity of greenish-brown crystals, having a golden metallic lustre. With a hot saturated solution of the base, the same sulphate is produced as an immediate crystalline precipitate. Dried over sulphuric acid, till constant, these two preparations gave the following results on analysis:—

I. ·4005 grm. substance gave ·14 grm. $BaSO_4$
II. ·6405 „ „ „ ·2175 „ „

These results correspond to the following percentages of sulphuric acid—

I.	II.
14·7	14·31

and accord well with the proportion of sulphuric acid contained in a compound of 2 eqs. of base and 1 eq. of acid—

$$(C_{20}H_{15}N_3)_2.H_2SO_4.$$

This formula requires 14·16 per cent. of sulphuric acid.

This sulphate dissolves in alcohol with a red colour; it is probable that the normal sulphate, $C_{20}H_{15}N_3,H_2SO_4$, is violet, like the corresponding chloride, when in solution. Attempts to isolate it have failed.

Boiled with hydrochloric acid for a day or two, azodinaphthyldiamine slowly decomposes, yielding hydrochlorate of naphthylamine, and an apparently new substance soluble in potash.

Action of Chloride of Benzoyl on Azodinaphthyldiamine.

Azodinaphthyldiamine, if our view of its constitution be correct, should contain but 1 eq. of replaceable hydrogen. Experiment has confirmed this opinion. If the dry finely-powdered base be heated with large excess of chloride of benzoyl for an hour, so that complete solution be effected, the liquid on cooling will become filled with brilliant dark-red crystals, which are not altered by a second treatment with chloride of benzoyl. They are easily purified from the hydrochloric acid produced but not disengaged in the reaction, from excess of chloride of benzoyl, and from any residue of unchanged substance, by treatment with potash, and repeated digestions with boiling absolute alcohol, in which the new product is nearly insoluble. The results of analyses of this derivative, are as follow—

I. ·2105 grm. sub. gave ·6205 grm. CO_2 and ·0945 grm. H_2O
II. ·176 „ „ „ ·523 „ „ ·0765 „
III. ·421 „ „ „ 37·28 cc. N. at 17° C., and 761·4 mm. Bar.

$$V' = \frac{37{\cdot}28 \text{ cc. } (761{\cdot}4 \text{ mm.} - 14{\cdot}4)}{807{\cdot}4} = 34{\cdot}51 \text{ cc. at } 0° \text{ C., and } 760° \text{ mm. Bar.}$$

34·51 cc. × ·0012577 grm. = ·043405 grm. N.

These results lead to the following percentages:—

	Experiment.			Theory.
	I.	II.	III.	($C_{27}H_{19}ON_3$).
Carbon	80·39	81·04	—	80·79
Hydrogen	4·98	4·83	—	4·74
Oxygen	—	—	—	3·99
Nitrogen	—	—	10·31	10·48
				100·00

These numbers agree almost exactly with those demanded by azodinaphthyldiamine, in which 1 eq. of hydrogen has been replaced by benzoyl. The formula of this substance, *benzoyl-azodinaphthyldiamine*, may be thus exhibited—

$$\left.\begin{matrix} C_{10}H_7 \\ N''' \\ C_7H_5O \\ C_{10}H_7 \end{matrix}\right\}N \quad = C_{27}H_{19}ON_3.$$

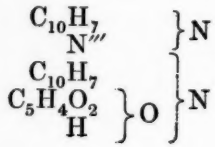
This benzoyl-substitution body presents in outward characters some resemblance to the original substance. Its chemical properties, however, are quite distinct. It is a very stable substance, capable of being fused without apparent decomposition. It is quite insoluble in water, but dissolves in boiling alcohol in just sufficient quantity to colour that liquid yellow. Hydrochloric acid, added in great excess to this solution, reddens and darkens the tint, but does not produce the least approach to a violet colour. Benzoyl-azodinaphthyldiamine dissolves in sulphuric acid with an intense blue colour. It is nearly insoluble in ether, but may be crystallised from benzol, in which it is slightly soluble, or from chloride of benzoyl. Alcoholic soda or potash dissolves it, yielding an orange solution, from which the benzoyl-body may be precipitated unchanged by the addition of water. It then appears as an orange-yellow powder. Continued ebullition with hydrate of potassium solution, followed by the action of hydrochloric acid, effects a partial decomposition of this remarkably permanent benzoylated base.

With other chlorides, such as those of acetyl and cumyl, similar derivatives to that obtained with chloride of benzoyl are produced.

When an alcoholic solution of azodinaphthyldiamine is mixed with hydrochloric acid and granulated tin added, it gradually loses its colour. When the tin has been removed by means of sulphuretted hydrogen, the filtrate, if evaporated to dryness, yields the hydrochlorate of one or more new bases, possessing peculiar characters. This reaction is now undergoing investigation.

Azodinaphthyldiamine, when mixed with anhydrous citraconic acid, dissolves, forming a deep purple liquid, which rapidly acquires

a yellow-brown colour. From the product, the excess of anhydrous citraconic acid is removed by repeated washings with water. The solid residual substance, which has acid properties, dissolves in caustic potash, and is reprecipitated unchanged by acids. It yields, when digested with alcohol and hydrochloric acid, azodinaphthyldiamine. We have not submitted this body to ultimate analysis, but in accordance with its mode of formation and properties, it is doubtless the citroconamic acid of the series. We may, therefore, predict for it the formula—



Azodinaphthylcitraconamic acid.

XXV.—*On the Derivatives of Hydride of Heptyl.*

By C. Schorlemmer, Assistant in the Laboratory of Owens College, Manchester.

Some years ago, Berthelot showed that, by the action of chlorine, on marsh gas, chloride of methyl is formed, from which, by double decompositions, other methyl-compounds can be obtained.* This method is a general one, and is applicable to all the hydrocarbons which are homologous with marsh gas, and I have already stated in a former communication,† that in this way I obtained *acetate of heptyl* and *heptylic alcohol,* from the corresponding hydride which I had previously found in the light oils from cannel-tar, and in larger quantities in rectified American petroleum. The constitution of this petroleum is, as I have shown in a communication read before the Literary and Philosophical Society of Manchester,‡ analogous to that of the oils from cannel-coal, inasmuch as it consists chiefly of the hydrides of the alcohol-radicles, but also contains benzol and homologous hydrocarbons.

The hydride of heptyl from petroleum, possesses in every respect

* Compt. rend., xlv, 916. † Chem. Soc. J., xv, 419.

‡ Proceed. Lit. Phil. Soc., Manchester, March 13, 1863.

identical properties with that from cannel tar; it boils at 98° C., the specific gravity is 0·7122 at 16° C.

Analysis: 0·1935 substance gave 0·5955 CO_2, and 0·2810 H_2O.

	Calculated.	Found.
C_7	84	83·93
H_{16}	16	16·13
	100	100·06

Determination of vapour-density—

Balloon with air.....	40·7955
Temperature of air	11° C.
Balloon with vapour	41·0960
Temperature of sealing....	173° C.
Capacity of balloon	189·0 cbc.

These numbers give the vapour-density = 3·59; the theoretical density of hydride of heptyl = 3·46.

The hydride was converted into the chloride according to the beautiful method of Hugo Müller,* care being taken to avoid an excess of chlorine; the unattacked hydride was then distilled off, and the chloride of heptyl, $C_7H_{15}Cl$, was obtained from the portion boiling between 140—160°, by fractional distillation, as a colourless liquid boiling at 150°C.

When bromine is added to hydride of heptyl, and the mixture is exposed to direct sunlight, or heated in sealed tubes in the water-bath, hydrobromic acid is slowly evolved; but the action is much less energetic than in the case of chlorine; it may, however, be quickened by adding a little iodine. As soon as the colour of bromine had disappeared, the liquid was subjected to distillation; a large quantity of hydride passed over first; the temperature then rose slowly; and as soon as it reached 110° C., the residue in the retort began to decompose, hydrobromic acid being given off, and a black charry matter left in the retort.

In order to convert the chloride of heptyl into the acetate, I heated it in sealed tubes with acetate of potassium and alcohol to 120°—130° C. The greater part of the chloride is decomposed in a few hours, but in order to remove the last traces of chlorine

* Chem. Soc. Journ., xv, 41.

from the liquid, the mixture has to be heated to 200° C. for several days; in this part of the operation the tubes were nearly always found to explode.

I afterwards replaced the alcohol by glacial acetic acid, and found, that by heating the tubes in the air bath to 150°—160° C. for twelve hours, all the chloride of heptyl was decomposed. The products are in both cases the same, namely, chloride of potassium, acetate of heptyl, and heptylene. The contents of the tubes were diluted with water; the light oily liquid which separated, was dried over chloride of calcium; and the heptylene, which boils at 95° C., easily separated by fractional distillation from the acetate of heptyl, boiling at 179°—181° C. The latter is a colourless liquid of a pleasant smell, resembling that of pears. Analysis gave the following results:—

I. 0·2185 grm. substance gave 0·5470 CO_2 and 0·2245 H_2O.
II. 0·2445 grm. substance gave 0·6105 CO_2 and 0·2570 H_2O.

	Calculated.		Found.	
			I.	II.
C_9	108	68·35	68·28	68·09
H_{18}	18	11·39	11·41	11·67
O_2	32	20·26	—	—
	158	100·00		

Distilled with a concentrated solution of potash, the acetate is decomposed, heptylic alcohol being formed. Heptylic alcohol $C_7H_{16}O$ is a colourless oily liquid, lighter than water, boiling at 164°—165° C., and possessing a peculiar smell, which reminds one both of octylic and amylic alcohols.

The analysis of heptylic alcohol gave the following results:—

I.—0·2035 substance taken
0·5390 CO_2 obtained
0·2625 H_2O „
II.—0·2445 substance taken
0·6480 CO_2 obtained
0·3115 H_2O „

	Calculated.		Found.	
			I.	II.
C_7	84	72·40	72 23	72·28
H_{16}	16	13·80	14·33	14·15
O	16	13·80	—	—
	116	100·00		

The acetate of heptyl and heptylic alcohol, which Bouis and Carlet obtained by the action of zinc and acetic acid on œnanthol,* possess the same boiling points as those I prepared from hydride of heptyl. It is noteworthy that the boiling-point of the acetate is about 10° higher, and that of the alcohol 10° lower, than the boiling-points calculated according to Kopp's law.

The action of iodine and phosphorus on heptylic alcohol yields the iodide of heptyl, a colourless liquid, heavier than water, which soon becomes brown in contact with the air, and boils at about 190° C. An alcoholic solution of nitrate of silver immediately decomposes it, and all the iodide separates out as iodide of silver, as the first of the following analyses shows.

I. 0·1695 iodide of heptyl was dissolved in alcohol, and an alcoholic solution of nitrate of silver added. It yielded 0·1490 AgI and 0·0125 Ag.

II. 0·3340 substance gave 0·4555 Co_2 and 0·2025 H_2O.

	Calculated.		Found.	
			I.	II.
C_7	84	37·17	—	37·19
H_{15}	15	6·64	—	6·73
I	127	56·19	56·18	—
	226	100·00		

A concentrated aqueous solution of potash scarcely acts upon chloride of heptyl, even if they are heated together in sealed tubes to 180° C. for several days. Only a small quantity of heptylene is produced, and not the least trace of heptylic alcohol is formed.

Heptylene C_7H_{14} is a colourless mobile liquid lighter than water, of rather a strong somewhat garlic-like smell, and boiling at 95° C.

0·2060 substance gave 0·6470 CO_2 and 0·2585 H_2O.

* Compt. rend., lv, 140.

	Calculated.		Found.
C_7	84	85·71	85·66
H_{14}	14	14·29	14·00
	98	100·00	99·66

With bromine it forms bibromide of heptylene $C_7H_{14}Br_2$, a liquid heavier than water, which decomposes on distillation, with evolution of hydrobromic acid and blackening, but volatilizes in presence of aqueous vapour, and condenses as a nearly colourless liquid, smelling like bibromide of ethylene, and having the above composition, as the following determinations of the amount of bromine show :—

I. 0·2590 substance gave 0·3665 AgBr and 0·0072 Ag.

II. 0·3555 substance gave 0·5020 AgBr and 0·0105 Ag.

	Calculated.		Found.	
			I.	II.
C_7	84	32·56	—	—
H_{14}	14	5·43	—	—
Br_2	160	62·01	62·26	62·23
	258	100·00		

Heptylene also combines with hydriodic acid, on heating them together in sealed tubes to 100° C. for twelve hours. The hydriodate of heptylene $C_7H_{14}HI$ closely resembles iodide of heptyl, but boils at about 170° C. or 20° lower; it readily turns brown in the air.

0·3290 grm. of hydriodate of heptylene was precipitated by an alcoholic solution of nitrate of silver, and gave 0·3230 AgI and 0·0075 Ag, corresponding to 55·73 % of iodine, instead of the calculated 56·19 %.

A larger quantity was treated in the same way, and the filtered liquid diluted with water. A small quantity of a liquid, lighter than water, and of a pleasant smell was obtained, which certainly consisted of, or at least, contained a large proportion of nitrate of heptylene C_7H_{14},NO_3H, as by adding an alcoholic solution of potash, and gently heating, an abundant precipitate of nitrate of potassium was formed.

A concentrated solution of ammonia in alcohol decomposes the

chloride but slowly, even if heated in sealed tubes to 120° C. for several days. The chlorides of the different heptyl-ammoniums are formed, but chiefly chloride of heptylammonium, a salt readily soluble in water and alcohol, and crystallising from solution in small scales. On distilling it with a solution of caustic potash, heptylamine $C_7H_{17}N$ is obtained as a light oily liquid, with an ammoniacal, aromatic smell, possessing a burning taste, and boiling at 145°–147° C. It is tolerably soluble in water, and separates out again on addition of caustic potash.

Analysis I.—0·2160 substance gave 0·1880 metallic platinum, corresponding to 0·0266 of nitrogen.

II.—0·1450 substance gave 0.3870 CO_2 and 0·2000 H_2O.

	Calculated.		Found.	
			I.	II.
C_7	84	73·04	—	72·79
H_{17}	17	14·79	—	15·32
N	14	12·17	12·31	—
	115	100·00		

The platinum-salt is slightly soluble in cold water, freely soluble in hot water, and dissolves readily in alcohol and ether, crystallising from those solutions in small yellow scales.

0·3795 of the double salt gave 0·1165, or 30·69 % Pt.
0·2800 gave 0·0860 or 30·71 % Pt.

The formula $C_6H_{18}NCl.\ PtCl_2$ requires 30·79 % of platinum.

XXVI.—*On the Hexyl-Group.*

By J. Alfred Wanklyn, Professor of Chemistry in the London Institution; and Dr. E. Erlenmeyer, Extr. Professor of Chemistry in the University of Heidelberg.

In the autumn of 1861, we laid before the Royal Society an account of the transformation of mannite into iodide of hexyl, and called attention to certain peculiar characters offered by that iodide. In particular we mentioned how very strangely it

behaves with alcoholic solution of potash, when, instead of giving an alcohol or an ether, it splits up into hexylene and hydriodic acid—the latter of course re-acting upon the potash. We remarked further, that the alcohol of the series obtained from oxide of silver, water, and the iodide of hexyl, did not smell at all like amyl-alcohol, and, referring to the very unsatisfactory account of the hexyl group given by Faget,* we intimated our intention of engaging in a thorough investigation of the series.

With that investigation we have been occupied for some time back. Our research is not yet finished, but a recent publication by M. Wurtz, in the *Comptes rendus*, induces us to publish our results just as they stand at the present time.

Since our first publication, a hexylic alcohol has been obtained by MM. Cahours and Pelouze from American oil, and this hexylic alcohol differs totally from ours. While ours offers unusual, abnormal characters, the hexylic alcohol of MM. Cahours and Pelouze presents the regular, well-known characters which are commonly ascribed to the vinic series of alcohols. Thus the interesting result is brought to light, that there are isomeric monatomic alcohols, and also isomeric derivatives of those alcohols.

We propose to designate the sets of compounds represented by the iodide of hexyl obtained from mannite, and by the derivatives obtained from that iodide, by the prefix β. To be consequent, it will be obvious we should prefix α before the ordinary normal fermentation-alcohols and their derivatives. By this procedure we desire to express that we look upon our new compounds as monatomic alcohol-compounds, but that we regard it as premature to offer any explanation of the difference between these and the usual alcoholic compounds.

M. Wurtz has recently found that the iodide of amyl obtained by exposing amylene to the action of hydriodic acid differs essentially from the common iodide of amyl produced by acting upon fusel oil with iodine and phosphorus. Like our iodide of hexyl, it tends to split up into the olefine and hydriodic acid. Like our hexylic alcohol, the abnormal amylic alcohol does not smell like fusel oil; like our hexylic alcohol, the abnormal amylic alcohol boils lower than the theory would indicate, and in short there is every reason to believe, that the compounds which M. Wurtz has

* Compt. rend., xxxvii, 730.

been investigating, are the homologues of the compounds which we have prepared from mannite.

M. Wurtz proposes to consider the new series as belonging to the glycol-compounds, and names them in accordance with this idea. We, on the contrary, as aforesaid, regard them as belonging to the monatomic class. Our reason is, that they exhibit only *one* replaceable atom. We can replace the iodine in iodide of hexyl by a great variety of radicles—by HO, by NaO, by $C_6H_{13}O$, by Br, by H.

If the bodies were of the glycol class, we should expect to find two replaceable atoms which we could readily replace by other radicles, but nothing of the sort is to be seen.

We would finally, before proceeding to describe our experiments, ask M. Wurtz, how it comes to pass that the admitted glycol-compounds do not exhibit that tendency to evolve the olefine which has induced him to regard the abnormal alcohols as belonging to the glycol series?

β. Iodide of Hexyl.

$$\beta C_6H_{13}I.$$

Preparation.—24 grm. of mannite are boiled in a spacious retort with 300 cub. cent. of strong aqueous hydriodic acid (boiling point 126° C.). During the boiling, a brisk stream of carbonic acid should be passed through the hot liquid in the retort, which is by this means kept well stirred up. The carbonic acid, moreover, carries over the iodide of hexyl as fast as it is produced, and thus preserves it from decomposition.

In about an hour, the operation is at an end, a distillate being obtained which consists of an upper layer of aqueous hydriodic acid holding iodine in solution, and a lower layer of dark-coloured iodide of hexyl. The lower layer is separated from the rest by means of a stop-funnel, and afterwards purified from free iodine by being shaken up with solution of sulphite of soda. After being thoroughly washed with water, it is still dark-coloured, notwithstanding that all free iodine may have been removed. In this state, however, the product is nearly pure—a rapid distillation in steam, which should be led into the retort, which is not directly heated with the lamp, suffices to render it colourless and (when dried with chloride of calcium) absolutely pure. When the above

operation is properly conducted, the quantity of product represents very fairly that which is required by this equation—

$$\underset{\text{Mannite.}}{C_6H_8(HO)_6} + 11HI = \underset{\text{Iod. Hexyl.}}{C_6H_{13}I} + 6H_2O + 5I_2.$$

96 grammes of mannite used in four operations gave 83 grammes of nearly pure iodide of hexyl. The above equation requires that—

96 grm. of mannite should give
111·8 grm. of $C_6H_{13}I$.

It should be mentioned, that it is not well to use more than 24 grammes of mannite at a single operation; further, the hydriodic acid and iodine remaining from an operation require only to be treated with sulphuretted hydrogen, decanted or filtered from the sulphur which separates, and boiled down till the boiling point reaches 126° C., in order to be fit for use in a fresh operation. This may be repeated several, but not an indefinite number of times, for gradually the acid becomes foul, and it is necessary to begin afresh.

Analyses of the iodide of hexyl have given the following results:—

I.—·4102 grammes burnt with chromate of lead and a little bichromate of potash, copper turnings being likewise employed, gave ·5119 grammes CO_2 and ·2286 grammes H_2O.

II.—·3878 grammes digested with alcoholic solution of sodium-alcohol, gave iodide of sodium, which furnished ·3975 grammes of AgI and ·0148 grammes of silver.

	Calculated.		Found.	
			I.	II.
C_6	72	33·96	34·03	—
H_{13}	13	6·13	6·19	—
I	127	59·91	—	59·87
	212	100·00		

Whence it appears, that the iodide was in a high state of purity.* We are thus warranted in the assertion, that the iodide

* In the instance of the alcohol-iodides low down in the series, ordinary elementary analysis may be reasonably invoked to decide upon the purity of a specimen; the percentage carbon-difference between iodide of hexyl and either of its neighbours is more than three.

of hexyl yielded by mannite, is free from any of its homologues, and, consequently, the derivatives obtained from it should, in like manner, be untainted by the presence of their homologues.

The specific gravity of iodide of hexyl is

1·4447 at 0° C.
1·3812 at 50° C.

Wherefore, the coefficient of expansion for 50° C. is 0·0460, or about $\frac{1}{4}$ that of gases. In the determination of specific gravity just given, and in all occurring in this paper, the standard taken is the weight of an equal volume of water at 4° C.; furthermore, unless special mention of the contrary is made, the results given require no correction for expansion of the glass bottle in which the determinations are made.

Iodide of hexyl boils at 167·5° (corrected) under a pressure of 752 mm. During the boiling, it undergoes only a very small amount of decomposition, but this slight change, nevertheless, renders the accurate observation of its boiling point difficult. The amount of decomposition which takes place on distilling has been made the subject of experiment. It does not seem to affect more than one or two per cent. of the iodide distilled. When, however, the crude iodide of hexyl, previously to its purification by distillation in steam, is distilled, great decomposition takes place.

Pure iodide of hexyl is tolerably stable. It is but very slowly coloured by exposure to the light. When hermetically sealed it is very slowly decomposed at a temperature as high as 230° C. It then becomes deep-coloured, from liberation of free iodine, but evolves no gas.

In smell, it resembles iodide of amyl; it is very insoluble in water, and requires rather more than an equal volume of absolute alcohol to dissolve it; the addition of even a very little water, renders a much greater volume of the solvent necessary to effect solution. It is also soluble in strong acetic acid and in ether.

The reactions of iodide of hexyl differ much from those of the common iodides of the alcohol-radicles. In every instance hexylene is evolved, but in very few cases is the hexylene unaccompanied by other organic products. Furthermore, it is extremely difficult to decompose the last traces of the iodide, the products of reaction seeming to be very potent in protecting them from decomposition.

Alcoholic solution of Caustic Potash gently warmed with iodide of hexyl, gives hexylene according to the equation,

$$C_6H_{13}I + KHO = C_6H_{12} + H_2O + KI.$$

The main reaction takes place according to this equation, but it is probable that small quantities of other organic products are produced at the same time, and to explain their production, other equations will be required.

Sodium-alcohol reacts very similarly to alcoholic solution of caustic potash.

Water decomposes iodide of hexyl into hexylene and hydriodic acid, at a temperature of about 190° C. We succeeded in decomposing a considerable proportion of the iodide into these products; but although we changed the water, and continued the heating for a long time, we did not succeed in converting the whole of a specimen of iodide of hexyl into hexylene and hydriodic acid. It seemed that the hexylene protected a certain proportion of iodide from the action of the water.

Acetic Acid.—Four volumes of nearly absolute acetic acid dissolved one volume of the iodide, giving a perfectly homogeneous liquid, which, when heated in a hermetically-sealed tube to 160° C., underwent no apparent change.

Acetate of Lead added to the solution of iodide of hexyl in acetic acid, and heated in a retort, gave abundance of iodide of lead, but no acetate of hexyl was detected. The only organic product which was with certainty detected, was hexylene.

Mercury acts upon the iodide in sun-light. Much iodide of mercury is formed, and a volatile liquid boiling at about 70° C., results. No gas is evolved. The reaction is this—

$$(C_6H_{13}I)_2 + Hg = HgI_2 + C_6H_{12} + C_6H_{14}.$$

Sodium begins to act at common temperatures, giving the well known blue iodide of sodium. In our experiment we sealed up the materials, and pushed the reaction further by heating in the water-bath. On opening the tube, we found a considerable quantity of hydrogen gas, a liquid boiling at 70° C., and undecomposed iodide of hexyl. No other product was detected. The fraction boiling at about 70° C., consisted of hexylene and hydride of hexyl, for a part of it was soluble in sulphuric acid, and the residual insoluble portion had the smell of hydride of hexyl. Two

reactions seem to take place side by side, when sodium acts upon iodide of hexyl—

$$(1.)\quad (C_6H_{13}I)_2 + Na_2 = C_6H_{12} + C_6H_{14} + (NaI)_2.$$
$$(2.)\quad (C_6H_{13}I)_2 + Na_2 = (C_6H_{12})_2 + H_2 + (NaI)_2.$$

Oxalate of Silver, whether air-dried or mixed with water or mixed with ether, gives abundance of hexylene by its reaction upon iodide of hexyl. We heated the mixture in the water-bath, for the reaction does not take place with particular readiness. Oxalic acid, in the free state, was found in the residue after the experiment. The change may be expressed by this equation—

$$(C_6H_{13}I)_2 + \left.\begin{matrix}C_2O_2''\\Ag_2\end{matrix}\right\} O_2 = \left.\begin{matrix}C_2O_2''\\H_2\end{matrix}\right\} O_2 + (C_6H_{12})_2 + (AgI_2.)$$

At the same time other reactions occur, for we detected hexylic alcohol among the products of the reaction.

Zinc and *Water*, and iodide of hexyl, sealed up together, and heated to 160° or 170° C., gave hexylene and hydride of hexyl.

Zinc and *Alcohol* and iodide of hexyl, heated together to 100° C., also gave hexylene and hydride of hexyl. Inasmuch as in both cases the quantity of hydride of hexyl obtained, fell short of one-half of the quantity that would have been given if all the iodide of hexyl had been converted into hydride of hexyl, we may represent the change by the equation—

$$(C_6H_{13}I)_2 + Zn = C_6H_{12} + C_6H_{14} + ZnI_2.$$

Oxide of Silver and *Water* give, with iodide of hexyl, a very complicated reaction. A considerable portion of the iodide of hexyl gives hexylene, thus—

$$(C_6H_{13}I)_2 + Ag_2O = (C_6H_{12})_2 + H_2O + (AgI)_2.$$

Another portion yields hexylic alcohol, thus—

$$C_6H_{13}I + AgHO = C_6H_{14}O + AgI;$$

and a further not inconsiderable proportion, gives a body which has the composition of hexyl-ether, thus—

$$(C_6H_{13}I)_2 + Ag_2O = (C_6H_{13})_2O + (AgI)_2.$$

Lastly, a portion of the iodide of hexyl resists decomposition with the greatest obstinacy.

Bromine acts upon iodide of hexyl in a very interesting manner; 10·6 grm. of pure iodide were treated with 6 grm. of bromine (1 equiv. $C_6H_{13}I$ to $1\frac{1}{2}$ eq. Br.), the bromine being gradually dropped into the iodide. Violent action occurred, solid iodine separated, and a liquid having at 11° C. a specific gravity of 1·375 was the result. From the specific gravity of this resulting liquid, it follows that the reaction cannot mainly consist in the generation of the body $C_6H_{12}Br_2$, for if the bromine had expended itself upon iodide of hexyl, so as to replace both hydrogen and iodine, we ought to have obtained a mixture of undecomposed iodide of hexyl and bibromide of hexylene. The specific gravity of such a mixture is higher than the specific gravity of our product. It is, therefore, obvious that a considerable portion of the iodide of hexyl must have had only its iodine replaced by bromine, and that the following equation represents one of the main changes—perhaps the entire first stage—

$$C_6H_{13}I + Br = C_6H_{13}Br + I.$$

We attach great importance to this reaction: for it shows very distinctly, that the atom of iodine is far more exchangeable than any of the hydrogen-atoms, and therefore that our iodide of hexyl belongs rather to the *vinic* than to the *glycolic* series.

Hexylene C_6H_{12}.

Preparation.—β Iodide of hexyl is heated in the water-bath, with an excess of potash and alcohol. The product is diluted with water, when the hexylene separates, and comes to the surface. After a little washing, it is dried with chloride of calcium and distilled, when it is obtained very nearly pure.

Its boiling point lies between 68° and 70° C. It is a very mobile fluid, lighter than water, and resembling amylene in smell. Its vapour-density was found in one experiment to be 2·88, and in another 2·97. (The formula C_6H_{12} requires 2·902?.)*

With *bromine* it unites with great violence, forming bibromide of hexylene.

Its behaviour towards *sulphuric acid* is very interesting. Mixed

* These determinations of vapour-density have been previously published in the Proceedings of the Edinburgh Royal Society, and are correctly copied into the Annles de Chimie et de Physique and into the gahres-bericht.

with sulphuric acid (strength = 99·3 per cent. of SO_4H_2) it combines with great energy. The mixture becomes hot, so that the hexylene boils, and at the same time assumes a red-brown colour, and evolves traces of sulphurous acid. On diluting the product with water, a thick oily liquid separates, which has the composition of *parahexylene*.

If, on the other hand, the sulphuric acid be diluted with about one-third of its volume of water, and then be shaken up with hexylene, combination takes place more slowly, and β hexyl-sulphuric acid is obtained. No sulphurous acid is evolved, and at most only a slight yellow tinge is given to the liquid. If, soon after this compound has been prepared, water be added to it, there will separate an oil which is not parahexylene, but β hexylic alcohol, identical with that which is produced by the action of oxide of silver and water upon iodide of hexyl.

Moreover, the aqueous liquid is found to contain *hexyl-sulphuric acid*; it yields hexyl-sulphates when treated with alkalis, and when boiled alone, it evolves β hexyl-alcohol.

Hydriodic acid and Hexylene.—An excess of aqueous hydriodic acid (boiling point 126° C.), sealed up with hexylene, and heated to 170° C. for some hours, gives β iodide of hexyl (boiling point about 165° C. at 753 mm. pressure). We thus see how important an influence the exact conditions have upon these reactions, for we found that *water in excess* resolved β iodide of hexyl into hexylene and hydriodic acid.

Hydrobromic Acid (sp. gr. 1·37) appears to unite with hexylene very slowly.

Bibromide of Hexylene,

$$C_6H_{12}Br_2,$$

is obtained by dropping bromine into hexylene, when combination takes place with extreme violence—with hissing and spitting. Only a very slight excess of bromine should be taken, and the liquid should then be shaken up with dilute caustic potash and dried. So prepared, the bibromide of hexylene is a heavy oily liquid. A remarkable property which it possesses is this: it forms crystalline compounds with certain inorganic salts.

Analyses of the bibromide were made—

I. 0·1659 grm., burnt with chromate of lead, gave 0·1750 carbonic acid (the water was lost).

II. 0·1349 grm. gave 0·1432 grm. of carbonic acid and 0·0645 grm. of water.

	Calculated.		Found.	
			I.	II.
C_6	72	29·51	28·77	28·95
H_{12}	12	4·92	—	5·31
Br_2	160	65·57	—	—
	244	100·00		

β. Hexylic Alcohol,

β. $C_6H_{14}O$

may be prepared either by the action of oxide of silver and water upon β iodide of hexyl, or by the action of sulphuric acid upon hexylene. Whichever way be adopted, the product is identically the same. Portions of alcohol prepared by these two processes, have been found to have the same composition, same boiling point, and same smell. When the first method is adopted, a poor product is obtained, for, as we mentioned above, part of the iodide is resolved by oxide of silver and water into hexylene, and part into hexyl-ether. Moreover, a small quantity of iodide of hexyl remains in the hexyl-alcohol, and can hardly be removed by means of oxide of silver and water. The best way to get rid of this last trace of iodide of hexyl, seems to be to digest with a little caustic potash.

The second method is by far the most convenient. Hexylene is shaken up with an equal volume of sulphuric acid (strength about 87 per cent. of SO_4H_2) when combination takes place in about a quarter of an hour. If combination be too tardy, it is well to drop in a little very concentrated sulphuric acid. As soon as the liquids have combined, twenty or thirty volumes of water should be added, and the whole distilled in a spacious retort. Pure β hexylic alcohol distils over.

β hexylic alcohol, after drying with anhydrous sulphate of copper, boils at 137° C. (corrected) under a pressure of 755·5 mm.

Its specific gravity at 0° C. = 0·8327
at 16° C. = 0·8209
at 99° C. = 0·7482*

* In this instance the correction for the expansion of glass was not made. It would increase the expansion-coefficient of the liquid.

The expansion-coefficient is rather high; 100 volumes at 0° C., become about 112 at 100° C., or β hexyl-alcohol expands about one-third as much as do gases.

I. 0·1476 grm. of β hexylic alcohol, gave 0·3800 grm. of CO_2 and 0·1835 grm. of H_2O.

II. 0·2453 grm. burnt with chromate of lead and bichromate of potash, gave 0·6296 grm. of carbonic acid, and 0·3064 grm. of water.

	Calculated.		Found.	
			I.	II.
C_6	72	70·59	70·21	70·00
H_{14}	14	13·73	13·84	13·88
O	16	15·68	—	—
	102	100·00		

β hexylic alcohol is an oily, not very mobile liquid. Its smell is refreshing and pleasant, and not at all like that of amylic alcohol. Sodium attacks it, evolving hydrogen, and forming a mass which is a jelly at 100° C., and a solid at ordinary temperatures. The solid (no doubt an alcoholate of soda) regenerates β hexyl-alcohol when treated with water.

Bromine attacks the alcohol with great violence.

Bichromate of Potash and *Sulphuric acid* attack β hexylic alcohol very readily, giving a liquid which has a very pleasant, fruity, but sharp smell.

Sulphuric acid gives hexyl-sulphuric or parahexylene, according to the way in which it is added to β hexyl-alcohol. If the experiment be made in the manner in which Wurtz operated upon his β amyl-alcohol, then only parahexylene is obtained, but by altering the circumstances, hexyl-sulphuric acid is produced.

The importance of this reaction, induces us to extract from our note-book a precise account of our experiments:—

I. 0·600 grm. of β hexylic alcohol was cooled down to 0° C., and then mixed with double its volume of concentrated sulphuric acid, also cooled down to 0° C. A clear homogeneous thick oily liquid resulted. The liquid was only slightly yellow. Bye and bye it became turbid. It was left to itself all night; next morning, a clear liquid floated on the sulphuric acid. The liquid was diluted with about 10 vols. of water, and the oil separated from the aqueous solution. This oil had the composition of an olefine, and reacted violently with bromine. It was undoubtedly parahexylene.

The aqueous liquid contained sulphuric, but not a trace of hexylsulphuric acid.

II. When weaker sulphuric acid is taken, or perhaps when a long time is not allowed to elapse before diluting the compound of sulphuric acid with β hexyl-alcohol, then an acid liquid is obtained, from which hexyl-sulphates have been prepared. It is to be presumed that the salts produced in this way are the same as those obtained directly from hexylene and sulphuric acid.

β. Hexyl-sulphuric Acid,

$$\beta.\ \left.\begin{matrix} C_6H_{13} \\ H \end{matrix}\right\} SO_4,$$

is obtained as aforesaid, by shaking up hexylene with sulphuric acid (strength 87 per cent. of SO_4H_2) and diluting the product with about 5 vols. of water. The aqueous liquid was separated by means of a stop-funnel from the β hexyl-alcohol, which floated above it. The clear aqueous liquid was treated with excess of carbonate of potash, evaporated to dryness in the water-bath, and the residue extracted with alcohol. The alcoholic solution of β hexyl-sulphate of potash was filtered, evaporated almost to dryness in the water-bath, and finished over sulphuric acid.

0·2702 grm. of dry residue left, on ignition, 0·1317 grm. of sulphate of potash. Although this residue of K_2SO_4 is considerably over what the formula $C_6H_{13}KSO_4$ requires, yet the fact of getting a potash-salt under these circumstances, which was so rich in organic matter, goes a great way to prove the existence of hexyl-sulphuric acid.

Another portion of the clear liquid was converted into a barium-salt which was soluble in alcohol of 95 per cent. Some of the barium-salt (dried in the water-bath) gave, on ignition, 45·4 per cent. of Ba_2SO_4. The formula $BaC_6H_{13}SO_4$, requires 46 per cent. of Ba_2SO_4.

Lastly, another portion of the clear liquid was distilled. It evolved β hexylic alcohol. The existence of β hexyl-sulphuric is, therefore, sufficiently established.

β. Hexylic Ether.

$$\beta.\ \left.\begin{matrix}C_6H_{13}\\C_6H_{13}\end{matrix}\right\}O.$$

Among the products of the action of wet oxide of silver upon β iodide of hexyl, a considerable quantity of liquid of very high boiling point is observed. This liquid, which is very difficult to separate from traces of β iodide of hexyl, seems to be the ether of the series. At first, large quantities of iodine were found in the liquid, and the carbon was as low as 61 per cent. After heating for a long time in a stream of carbonic acid, so as to drive off the iodide of hexyl, the carbon rose to 68 per cent., and lastly to 76 per cent. When the carbon had risen as high as this last figure, we could no longer detect iodine in the compound. The question seemed to us to be whether the liquid of high boiling point was the ether or parahexylene. If it had been parahexylene we should certainly have been able to push the fractionation further, so as to have got more than 76 p. c. of carbon (parahexylene contains 85·7 p. c. of carbon).

The liquid which we take to be β hexyl-ether boils constantly between 203·5° C. and 208·5° C. (corrected) at 751 mm. pressure. It is a thick, slightly yellow liquid, of a faint penetrating smell.

Its analyses gave :—

	Calculated.		Found.	
			I.	II.
C_{12}	144	77·42	76·01	75·99
H_{26}	26	13·98	14·07	13·42
O	16	8·60	—	—
	186	100·00		

We shall repeat the investigation of this compound. The reaction of phosphorus, iodine, and water upon it is of great importance. If it be really the ether of the series, we should get β iodide of hexyl by such a process.

Hydride of Hexyl.

$$C_6H_{14}.$$

Hydride of hexyl may be obtained by heating together zinc, alcohol, and β iodide of hexyl. It is purified from hexylene by being shaken up with concentrated sulphuric acid, or by treatment with bromine. The yield is not very good. From 56 grammes of

β iodide of hexyl only 6·7 grammes of C_6H_{14} were obtained. If half of the iodide were converted into hydride, 11·3 grm. should have been produced.

The product, moreover, seemed to be not absolutely pure.

0·2736 grm. burnt with oxide of copper, chlorate of potash being used, gave 0·8247 grm. of carbonic acid, and 0·3970 grm. of water.

	Calculated.		Found.
C_6	72	83·72	82·21
H_{14}	14	16·28	16·12
	86	100·00	

Although the carbon-determination is too low (owing probably to the presence of a little β hexylic alcohol), yet the analysis is quite decisive for the formula: the hydrogen determination alone would settle this point.

We have prepared hydride of hexyl more than once, and have always hitherto obtained analytical results like the one given. It is our intention to prepare large quantities of hydride of hexyl, and to endeavour, by long digestion with sodium or with sulphuric acid, to remove the last traces of impurities.

The boiling point of our product was 68·5° C. to 70° C. Bar. = 753 mm. Sp. gr. at 16·5° C. = 0·6645, which is lower than that found by Cahours and Pelouze, or by Schorlemmer.

We would remark that no trace of impurity, which could possibly be present, would tend to increase the specific gravity of our hydride of hexyl.

The smell of our C_6H_{14} was fragrant. We find that bromine acts with the greatest difficulty upon hydride of hexyl. 6 vols. of C_6H_{14} were sealed up with 1 vol. of bromine and exposed to bright sunlight for many hours. No decolorization took place. Heated to 120° C., still no decolorization. Exposed again to sunlight, then decolorization took place slowly, and on opening the tube torrents of hydrobromic acid escaped.

The action of chlorine upon C_6H_{14} is also slow, but, by means of iodine the reaction can be effected with tolerable ease.

We are thus brought to the interesting question, Are there two hydrides, as there are two iodides of hexyl? We refrain from giving an answer at present. Our hydride is of lower specific gravity than the hydride of other observers, and towards bromine

it is far more passive than theirs. But the hydride of other observers was obtained from a mixture of its homologues, and, as any one may convince himself by reference to the original memoirs, may have contained abundance of impurities.

London, May 20, 1863.

XXVII.—*On a Curious Instance of Electrolytic Action.*

By F. A. Abel, F.R.S.

The inspection of a number of the lead-coated projectiles, employed with the Armstrong guns, has recently brought to light some curious and quite unexpected instances of the establishment of voltaic action within the coatings of certain of these projectiles, and in positions where the existence of an exciting cause was not at all anticipated.

It has been customary to attach the coating of soft-metal (which is an alloy of lead with a small proportion of tin or antimony) to the body of the cast-iron projectiles, by two different methods. The one consists in providing the iron surfaces with a number of grooves formed at somewhat acute angles with the surface; the soft metal with which these become filled when it is cast over the shot or shell, serves to attach the coating firmly to the body. The other method consists in first alloying and coating the surface of iron with zinc (by the so-called galvanising process), and then immediately covering it with the soft metal. The covering of zinc fixed, in this instance, upon the iron, becomes the medium by which the coating of lead-alloy is attached to the body of the projectile. By the latter method, therefore, a perfect juncture is accomplished between the two parts, while, by that first-named, they may be said to be fitted together accurately, or riveted together.

The different manner in which the iron and the lead-alloy are affected by considerable changes of temperature has led, in a few instances, of a very special character, to a distortion of the coatings which have been attached by the mechanical method (*i.e.*, by means of grooves) in consequence of their partial separation from the body of the projectiles. The alterations in form presented by some shells of this class, which have been exposed for a

time to the effects of considerable changes of temperature, differ, however, altogether from those exhibited by a small proportion, among a number inspected, of shells, the lead-coatings of which were attached by means of zinc. On various parts of these shells, the soft metal was found to have become raised in the form of blisters, varying in size from $\frac{1}{4}$ inch to 1 inch in diameter. A large (110-pr.) shell, which had been preserved officially, as a standard pattern, since November, 1861 (having been kept in a glass case), exhibited, upon its coated surface, in addition to numerous smaller blisters, one measuring 1·1 inch in diameter, and projecting $\frac{1}{4}$ inch beyond the surface of the shell. These projections, or blisters, were not confined to any particular position upon the different shells; neither had those projectiles, which exhibited them, been exposed to any considerable changes of temperature.

The only inference deducible from the appearance of these projectiles was, that the blisters had been produced in consequence of the generation of gas at those parts of the shells between the iron surface and the coating of soft metal, which gas had gradually accumulated to such an extent as to be placed under very considerable pressure, and, consequently, to exert, eventually, an amount of force sufficiently great to tear asunder the two surfaces of metal which had been joined by means of the zinc, and to raise up and expand the comparatively plastic alloy of lead. This influence was fully borne out by the following results of examination of the blisters.

When these were punctured, under water, a quantity of gas, existing evidently under considerable pressure, made its escape. The gas was separately collected from blisters upon different shells, and was found, in all instances, to consist of pure hydrogen.

The entire volume of gas, enclosed in the large blister specially referred to above, was carefully collected, and its volume was determined. The capacity of the blister was afterwards measured, and the results furnished by these determinations showed that the hydrogen existed at the period of examination, under a pressure very slightly exceeding ten atmospheres.

By carefully cutting through the metal surrounding the blisters, several, which had been otherwise operated upon, were removed from the shells, the internal surfaces remaining untouched. On a close inspection of these surfaces, they were all found to resemble each other closely, those of the blisters as well as those of the

iron body of the shell, immediately beneath them. They presented a frosted metallic appearance, small dark patches or spots, indicative of corrosion, being visible here and there. Those of the blisters and of the iron beneath were alike coated with zinc, and their peculiar appearance, just referred to, was to be ascribed to the existence, upon them, of numerous small projections, such as are observed upon the surfaces laid bare when a piece of metal is fractured by a tensile strain.

It is evident, from the foregoing details, that the projections, or blisters, which have been described, had been produced by the gradual disengagement of hydrogen between the body of the projectile and the coating of lead-alloy, whereby the two descriptions of metal, joined together thoroughly in the first instance (except probably at a few minute points) through the medium of zinc, had been torn asunder, and the thin intermediate zinc coating itself divided, the gas gradually creating further space for itself by expanding the envelope of soft metal which confined it.

That these results must have been due to the electrolytic decomposition of some hydrogen-compound, which had become enclosed between the metals, is self-evident; an examination into the process of manufactures of these projectiles, aided by a few simple experimental data, appears to leave no doubt regarding the primary cause of this disengagement of gas.

The operations included in the system of coating the iron projectiles by the aid of the so-called galvanising process, are as follow:—The cast-iron projectile, after having been turned, so as to present a perfectly clean metallic surface, is heated in an oven until its temperature approaches the fusing point of zinc; it is then plunged into a solution of sal-ammoniac, almost immediately withdrawn, and immersed in a bath of melted zinc, where it remains for about two minutes, when it is transferred to a bath of the lead-alloy with which it is to be coated. After remaining in this bath also for a period of two minutes, it is withdrawn and placed in a mould. The projectile thus treated has become uniformly covered with a thin coating of soft metal, the thickness of which is afterwards increased, by pouring a further quantity of the alloy round the coated projectile, directly it has been placed in the mould.

When the heated projectile is passed from the chloride of ammonium solution to the bath of zinc, portions of the salt remain adhering to the iron, upon its immersion in the zinc, and there

is no doubt that a small proportion of water may also, occasionally, be carried along with it, so as to be brought together with it into contact with the melted metal. A small proportion of chloride of zinc is always formed at this stage of the process, by decomposition of the chloride of ammonium, in consequence of the high temperature at which particles of this salt are brought into contact with the zinc, and with oxide of zinc, small portions of which may accidentally attach themselves, at the moment of immersion, to any slight inequalities on the surface of the iron. The remarkable tendency of chloride of zinc to absorb and retain water, even at very high temperatures (the latter being only gradually expelled from it, even at the temperature of melted zinc), renders it easily conceivable that, at the time of production of the zinc-salt, any water accidentally present, besides that which results from the decomposition of the ammonium-salt by oxide of zinc, will at once be absorbed by it; there is no doubt, therefore, that any particles of chloride of zinc accidentally enclosed by the zinc-coating formed upon the iron surface, will still retain some water at the expiration of the brief period during which they continue exposed to the high temperature of the zinc-bath. Afterwards, when the coating of zinc becomes, in its turn, speedily enveloped in that of the lead-alloy, the temperature of the projectile gradually diminishing up to the termination of the process, the escape, or decomposition, of the water, through the agency of heat, is speedily arrested.

Thus it is that portions of water become accidentally enclosed between the iron body and the zinc-coating of compound projectiles prepared by this system; and it is this enclosed water which afterwards suffers gradual decomposition through electrolytic agency; the accumulation of the liberated hydrogen giving rise, eventually, to the projections or blisters in the coating of soft metal.

The surfaces laid bare by carefully cutting open many of these blisters, invariably furnished proof that chloride of zinc had been enclosed at those places, and that a basic chloride had been formed. Water removed from them a mere trace of chlorine, but, by a brief treatment with dilute acetic acid, abundant evidence was obtained of the existence of a chloride within the blisters.

It should be observed that these accidental distortions of the lead-coating on Armstrong projectiles which have been prepared

by means of the galvanising process, appear not to be of frequent occurrence, and that they do not interfere with the efficiency of such projectiles, because, even in the most striking instances, they constitute only a very small proportion of the coating of soft metal, which is, in all other parts, inseparably joined to the iron; and also, because the coating may, in places where it has been raised in blisters, be restored to its original dimensions by simple mechanical means.

XXVIII.—*On the Iodide of Iodammonium.*

By Frederick Guthrie, Professor of Chemistry in the Royal College, Mauritius.

The symbol II is employed to express isotypism; the symbol III to denote idiotypism :* thus—

$$HCl \text{ III } KCl \text{ III } KI \text{ III } NaI, \&c.$$
$$HCl \text{ II } C_2H_3Cl \text{ II } C_{10}H_{11}I, \&c.$$
$$NH_3 \text{ II } NH_2C_2H_3 \text{ II } NH\,C_2H_3\,C_4H_5, \&c.$$

The explosive body produced by the action of aqueous ammonia upon iodine, sometimes called "iodide of nitrogen," has been shown by Bineau† to be an ammonia, in which two equivalents of hydrogen have been replaced by two equivalents of iodine—

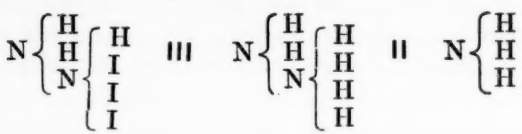
$$N\left\{\begin{matrix}H\\I\\I\end{matrix}\right. \text{ III } N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$$

By the action of ammonia upon an alcoholic solution of iodine, Bunsen‡ obtained a body, to which he assigned the formula

$$NH_3NI_3$$

* Chem. Soc. Qu. J., xiii, 35.
† Comptes rendus, xix, 764.
‡ Ann. Ch. Phys. lxxxiv., 1.

This formula may be brought under the same type*—



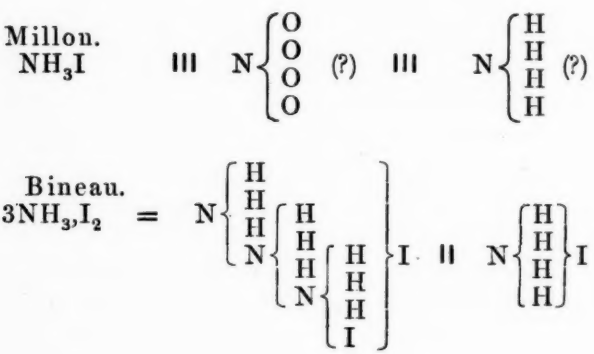
namely, by viewing it as an ammonia, in which one equivalent of hydrogen is replaced by an ammonium, in which three equivalents of hydrogen are replaced by three equivalents of iodine.

Yet Gladstone† finds, that the body produced by acting with ammonia upon an alcoholic solution of iodine has the composition assigned by Bineau to his compound.

The discrepancy in the results obtained by these chemists may arise from the difference in the conditions of their experiments, having given rise to bodies in reality differently constituted.

By the action of dry ammonia upon iodine, a body is obtained, to which Millon gives the formula NH_3I, and to which Bineau has given the formula $3NH_3.I_2$. The first of these formulæ would obviously be that of iodammonium, a body to which, with perhaps the exception of nitroxine, no antitype is known; the formula of Bineau is that of *iodide of iodammonammonammonium.*

Iodide of Ammonia.



* For a similar formulation of polynitrides, see Phil. Mag., September, 1857, p. 185.

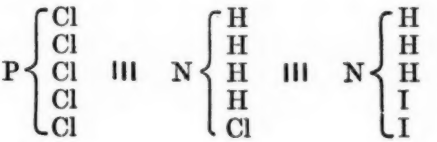
† Chem. Soc. Qu. J. v., 34; vii., 51.

The conditions under which iodine and ammonia are brought together, do therefore in truth greatly modify the composition and properties of the resulting product, and may, as will be shown immediately, give rise to a product different from all those above described.

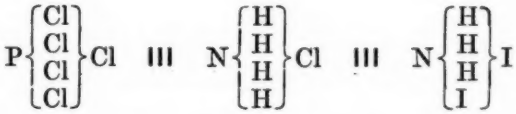
The new body has the composition—

$$NH_3I_2$$

being idiotypic with pentachloride of phosphorus or chloride of ammonium.



or,



This body, which may be called the *iodide of iodammonium*, is readily formed in the following manner. A saturated solution of some very soluble salt of ammonia (the nitrate or carbonate) is treated with about $\frac{1}{3}$rd of an equivalent of hydrate of potash, so that all the potash is neutralised, and the ammoniacal salt is in excess.* To the clear solution, finely powdered iodine is added in small quantities, with constant agitation. The iodine appears to be immediately and perfectly liquified; no appreciable heat is evolved. The iodine, in uniting with the elements of ammonia, presents itself as a thoroughly mobile brownish-black liquid. The supernatant saline solution remains almost colourless. A few bubbles of gas rise from the lower liquid and drag portions of it to the surface of the upper one. The iodine is used in deficiency to ensure its complete conversion. The iodide of iodammonium is separated by a pipette from the saline solution. Its properties are briefly as follow:—

* It is noteworthy, in its bearing upon Berthollet's law, that such a solution can be readily filtered through paper without affecting the latter, after the manner of even dilute caustic potash, so unequally are the bases shared, although both remain in the chemical field.

Exposed in the dry state to the air, it decomposes spontaneously into ammonia and iodine, no permanent gas being evolved. On agitating it in a eudiometer-tube with mercury, iodide of mercury is formed, and the mercury is depressed by the liberated ammonia, which latter is completely absorbed by water—

$$NH_3I_2 + 2Hg = NH_3 + 2HgI.$$

Treated with water, it is decomposed, colours the water reddish-brown, evolves a permanent gas, and gives rise to a residue which explodes spontaneously under water.

A few grammes of the iodide of iodammonium in a capsule being placed under water in a basin and covered with an inverted test-tube of water, a gas collects in the tube, which, after washing to remove ammonia, is found to be pure nitrogen:

$$\begin{aligned} 2NH_3I_2 + HO &= NHI_2 + NH_4I + HI + HO. \\ &= N + 2HI + I + NH_4I + HO \end{aligned}$$

The coloration of the water is due to the solution of the iodine in the hydriodic acid and iodide of ammonium.

The formation of the biniodammonia (iodide of nitrogen) is more rapid than its decomposition, so that some of it is left after the original compound is completely broken up.

The part which the water plays in this decomposition seems to be wholly due to its solvent power for hydriodic acid and iodide of ammonium. The water determines the formation of the things which it can dissolve, according to a well-known corollary of Berthollet's law. Doubtless, for the same reason, the decomposition of the body is stopped almost completely by the addition of saturated solutions of many neutral salts.

Comparing the decompositions wrought by water and air, it is seen that each medium effects the resolution of the compound into those constituents which most readily dissolve in the medium.

The caustic alkalies effect the same decomposition as water, but act more energetically, on account of the greater affinity of their metals for the iodine.

Acids determine the formation of ammonia—

$$\begin{aligned} NH_3I_2 + HCl &= NH_4Cl + I_2 \\ NH_3I_2 + HOSO_3 &= NH_4OSO_3 + I_2 \\ \text{\&c.} &\qquad \text{\&c.} \end{aligned}$$

The instantaneous recomposition of iodide of iodammonium by acids furnishes the means for its analysis.

Two or three drops of iodide of iodammonium are allowed to fall into a counterpoised flask containing dilute sulphuric acid. The increase in weight gives the amount of substance. The contents of the flask are agitated and thrown upon a filter. The separated iodine is washed with cold dilute sulphuric acid, converted, in the usual way, into iodide of potassium, and determined as iodide of silver. The sulphate of ammonium in the filtrate is converted into chloride of ammonium by the addition of chloride of barium, and the excess of barium being removed by sulphuric acid, the ammonia is determined by means of platinum.

I.—·7236 grms. of substance, and
II.—·6666 grms. of substance, gave—

	Calculated.		I.	II.
N =	14	5·17	4·88	5·43
H_3 =	3	1·10	1·04....	1·16 (calc.)
I_2 =	254	93·73	93·47	93·04
	271	100·00	99·39	99·63

When a saturated solution of iodine dissolved in iodide of potassium, is added to the mixed solutions of caustic potash and nitrate of ammonia, a similar and probably identical liquid is formed, which separates in minute oily drops. I did not succeed in collecting these drops in a satisfactory state for analysis.

To prove, therefore, that the above analysed iodide of iodammonium is not a mixture of two or more substances, it was submitted to fractional solution in the manner described in the Journal of the Chemical Society, vol. xiv, p. 128. The solvent used was chloroform, in which the iodide of iodammonium is only slightly soluble. Several grammes of the body having been about half dissolved in dry chloroform, ·5454 grms. of the residue were analysed as above, and gave—

N =	4·98
H =	1·07 (calc.)
I =	91·22
	98·27

Whence it is clear that the body is homogeneous.

The iodide of iodammonium dissolves in ether, bisulphide of carbon, alcohol, and solution of iodide of potassium.

On being heated, it is partly decomposed into iodine and an iodiferous liquid, which may be distilled without decomposition, and is most probably Millon or Bineau's "Iodide of Ammonia" formed according to one or other of the equations—

$$NH_3I_2 = I + NH_3I \qquad \text{(Millon)}$$
$$3NH_3I_2 = I_4 + 3NH_3.I_2 \qquad \text{(Bineau)}.$$

In conclusion, it may be remarked, that we might well, *a priori*, have predicted the probable existence of the iodide of iodammonium. Its formation is strictly analogous to that of the halides of ammonium by the union of ammonia with hydrhalides.

$$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + HI = N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right\}I$$

$$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + II = N\left\{\begin{matrix}I\\H\\H\\H\end{matrix}\right\}I$$

It may also be consistently presumed, that isotypes and idiotypes of the body may be formed, having other equivalents of hydrogen replaced by chemico-negative groups or elements.

XXIX.—*On Vanadium Ochre, and other Sources of Vanadic Acid.*

By Dr. T. L. Phipson.

In 1859, when M. Beauvallet announced the existence of small quantities of vanadic acid in the clay of Gentilly, near Paris, I

made several experiments upon a variety of Belgian clays, and almost always found small quantities of vanadium present; whilst my friend, Professor Pisani, in whose laboratory I was working, had procured some flower-pots from the Jardin des Plantes, known to have been made with the clay of Gentilly, but which yielded only minute traces of vanadic acid, even after boiling for many hours with carbonate of soda, according to M. Beauvallet's method.

The method I have adopted for extracting vanadic acid, and which is similar to that imagined by Sefström, is much more rapid and accurate than the one just alluded to. Instead of boiling with carbonate of soda, or with caustic soda, I calcine the substance with half its weight of saltpetre, and then treat with boiling water for a quarter of an hour; the vanadic acid is converted first into vanadate of baryta and finally isolated as vanadate of ammonia.

In clays I generally met with titanic acid and tantalic acid. The former has been noticed by Mr. Riley, and the latter by M. Terreil. I have also found both these substances in the residue left on dissolving argillaceous carbonate of iron in hydrochloric acid.

The substance I have called vanadium ochre, to distinguish it from other similar minerals, is a sort of bog-iron ore, which I obtained from Mr. Gregory, of London. This substance, which occurs in Saxony, has a very peculiar aspect; it is composed of small round grains of hydrated oxide of iron, of the size of millet seeds, perfectly solid, and held together by a ferruginous argillaceous cement. The whole is of a reddish-brown colour, approaching to purple, and gives a light yellowish-brown powder like that of some varieties of limonite. This mineral is, indeed, essentially composed of limonite, as will be seen in the subjoined analysis, but it contains nearly 2 per cent. of vanadic acid. When treated before the blow-pipe with the view of putting the vanadic acid in evidence, this mineral gives no re-action of vanadium, but distinctly that of titanic acid. This seems to indicate that in mineral substances containing titanic acid, it is not possible to obtain, with phosphorus-salt, the beautiful green pearl of vanadic acid, even when this substance is present in notable quantity. My analysis of this vanadium ochre gives :—

		Atomic ratio.
Water with a little organic matter..	12·60	
Ferric oxide.....	57·50	
Alumina	5·00	
Vanadic acid	1·90	0·0205
Phosphoric acid	2·20	0·0309
Titanic acid	traces	
Magnesia.....	0·30	
Lime.....	0·20	
Carbonic acid	0·24	
Silica (quartz) &c.	20·00	
	99·94	

The round hard grains which compose the mineral are pure limonite $\ddot{F}e_2\dot{H}_3$; all the vanadium, phosphoric acid, alumina, &c., are in the argillaceous cement which holds the grains together, and which can be separated completely by prolonged lixiviation. It will be seen by this analysis that the vanadic acid and phosphoric acid are exactly in the ratio of 2 : 3; so I doubt not that the compound of vanadium present in this vanadium-ochre is the phosphate $\ddot{V}d_2\ddot{\dot{P}}h_3$ described by Berzélius. This fact led me to suppose that in all iron ores and clays containing phosphoric acid I should probably meet with vanadic acid also. Such, as far as my experiments have gone, has been found to be the case, though I have not met with any ore in which vanadium is accidental, yielding a larger per centage of vanadic acid than the vanadium ochre of which the analysis appears above. The following are a few quantitative determinations I have made, to which I have appended some results obtained by others who have also sought for vanadic acid in mineral substances where it is accidental :—

Author.	Substance Examined.	Vanadic Acid per cent.
1. Phipson	London clay (London)	0 023
2. „	id. id.	0 056
3. „	Gault clay (Sussex)	0 046
4. „	id. id.	0 070
5. „	White clay (Ypres, Belgium) ..	0 033
6. „	Micaceous oligiste (English) ..	0 40 (much phosphoric acid)
7. „	Red hematite (English)	0 92 (id. id.)
8. „	Vanadium ochre (Saxony)	1 62 (id. id.)
9. „	id. id.	1 90 (id. id.)

Author.	Substance Examined.	Vanadic Acid per cent.
10. Phipson	Several other clays and hydrated oxides of iron	quantity not determined
11. Müller, A. ..	Limonite (Wüttemburg).....	0·03
12. Fritsche	Copper ore (Konichalcite containing phosphoric acid, arsenic acid, and lime)	1·78
13. Weibye.....	Silicate of alumina (Norway) ..	0·22
14. Schroetter ..	Iron slags (Verdenberg)	0·37
15. Kersten	Sulphide of iron slag	0·15
16. „	Copper-schist (Mansfeld).....	quantity not determined
17. Woehler .. Svanberg . Ficinus ..	Pitchblende (Germany)	„ „
18. Schultz .. Bodeman .	Iron ores	„ „
19. Sefström	Iron ore (Taberg, 1830. Discovery of Vanadium)	„ „
20. Beauvallet ..	Flower-pots made with clay of Gentilly (1859), France	„ „
21. Deville, H. ..	Bauxite (France).....	„ „
22. „ ..	Rutile	0·32

The preparation of vanadic acid upon the large scale from most of the above substances, especially pitchblende, and vanadium-ochre, is by no means a complicated process, and can often be effected without converting the acid into a baryta-salt. I have remarked that vanadate of ammonia at first yellowish-white, becomes, after remaining some days under water in an open vessel exposed to the light, entirely brown. This results from a constant loss of ammonia, and the gradual transformation of neutral vanadate of ammonia into bivanadate, supervanadate, and finally into anhydrous vanadic acid.

XXX.—*Note on the Detection of Arsenic in Copper.*

By William Odling, M.B., F.R.S.

As even in the most satisfactory performance of Reinsch's test for arsenic—the deservedly favourite test of English toxicologists—there is always some, although but an extremely small quantity of the copper wire, foil, or gauze dissolved, and as commercial copper is rarely quite free from arsenic, and sometimes contains a very notable proportion thereof, it is important that the copper to

be used in medico-legal researches as a precipitant for arsenic should be specially tested as to its purity.*

But, as in the ordinary mode of experimenting by Reinsch's process, the amount of metal dissolved is scarcely appreciable, it is quite unnecessary to submit any considerable quantity of it to examination. If a solution of four or five grains of the copper does not yield any evidence of arsenic, it is quite pure enough for the purpose, even though a little arsenic should be recognised in the solution of a larger quantity.

As a means of detecting traces of arsenic in copper, the author believes that the following process is superior to any hitherto proposed in conjoint delicacy and rapidity of operation.

A few grains of the copper, cut into fine pieces, are placed in a small tube-retort with an excess of hydrochloric acid and so much ferric hydrate or chloride as contains a quantity of iron about double the weight of the copper to be acted upon. The mixture is then distilled to dryness, some care being taken at the last to prevent spurting. The whole of the copper is in this way quickly dissolved, and any arsenic originally contained in it carried over in the form of chloride of arsenic, which may be condensed in a little water with the excess of aqueous hydrochloric acid. The resulting distillate is then tested for the presence of arsenic, by treating it with sulphuretted hydrogen, or, preferably, by boiling in it a fresh piece of clean copper foil or gauze. In some cases, the residue left in the retort may be treated with a little fresh hydrochloric acid, again distilled to dryness, and the distillate collected and tested along with that first produced.

Most oxygenants other than ferric chloride are objectionable, as by their reaction with hydrochloric acid they give rise to free chlorine which passes over with the distillate, and renders it unfit for being immediately tested either with sulphuretted hydrogen or fresh copper. Cupric oxide, or chloride on the other hand, is scarcely active enough for the purpose; while the dissolution of copper in hydrochloric acid brought about by mere exposure to the air is extremely tedious.

It may be as well to add that ferric chloride is rendered quite free from arsenic by evaporating it once or twice to dryness with excess of hydrochloric acid.

* Taylor—Guy's Hospital Reports [3], vi, 201; Abel and Field—Journal o Chemical Society, xiv, 291.

XXXI.—*On the Conversion of Prussic Acid into Methylamine.*

By Henry Debus, Ph.D., F.R.S.

According to Mendius,* hydrogen in the nascent state combines with the nitriles, and forms the primary monamines of the alcohol-radicles; with prussic acid, for example, methylamine. The important application which may be made of this base in practical chemistry, induced me to search for an easy and convenient method of preparing it, and, perhaps, the observations made during this investigation will not be devoid of interest to the Chemical Society.

Platinum-black, as is well known, induces oxygen and hydrogen to combine and form water, and therefore it appeared to me not improbable that the same agent might cause hydrogen and prussic acid to form methylamine. Experiment has confirmed my expectation.

Through a mixture of 15 grms. of cyanide of potassium, 15 grms. of sulphuric acid, and 5 ounces of water, contained in a retort, a stream of hydrogen was passed, and then conducted in succession, through an empty vessel, a tube containing fused chloride of calcium, a tube containing platinum-black, and finally through a Liebig's condenser filled with diluted hydrochloric acid. As soon as the mixture of prussic acid and hydrogen touched the platinum, dense white clouds became perceptible, which filled the apparatus from the platinum to the acid, and the tube containing the platinum became in some places so hot as to be unbearable to the touch. A trial experiment had shown a temperature of about 110°C. to be the most suitable for the accomplishment of the reaction, and therefore the tube with the platinum was immersed in a bath of paraffin of the temperature named. Oily drops, which condensed from the gases and vapours after they left the platinum tube, ran down the slightly inclined glass tube into the condenser containing the acid. The prussic acid mixture was gradually heated to the boiling point and kept at that temperature, with a current of hydrogen continually bubbling through it, until the experiment was finished. The acid fluid in the condenser, which smelt strongly of prussic acid, was evaporated

* Ann. Ch. Pharm., cxxi, 129.

on the water-bath. Thus a white residue, almost completely soluble in absolute alcohol, was obtained. The alcoholic solution left after evaporation a highly hygroscopic, colourless, crystalline mass—hydrochlorate of methylamine.

The platinum-salt of this substance appeared to be the most suitable compound for analytical operations. Accordingly, to the aqueous solution of the saline mass, bichloride of platinum was added as long as a precipitate formed; after this, the whole was heated to the boiling point. The yellow crystalline precipitate dissolved completely in the hot liquid. After filtration, the latter was allowed to cool slowly, when small groups of crystals radiating from a common centre, made their appearance. The mother-liquor gave a second crop of the same crystals, after suitable concentration. These crystals proved to be the platinum-salt of the hydrochlorate of methylamine. After two recrystallisations from boiling water, and drying over sulphuric acid, they were ready for analysis.

I. 0·098 grm. gave 0·041 grm. platinum.

II. 0·297 grm. of another preparation gave 0·124 grm. platinum.

0·1505 grm. gave 0·063 grm. platinum.

0·357 grm. burnt with chromate of lead, gave 0·0615 grm. carbonic acid and 0·0795 grms. water.

0·6015 grm. burnt with lime, gave 1·096 grms. chloride of silver and 0·006 grm. metallic silver.

100 parts of the substance therefore contain:

	I.	II.	
Carbon	—	.. 4·70	
Hydrogen ..	—	.. 2·47	
Platinum ..	41·83	.. 41·75	41·86
Nitrogen ..	—	.. —	
Chlorine ..	—	.. 45·38	

The formula $CH_5N.HCl + PtCl_2$ requires—

Carbon	1	12	5·06
Hydrogen	6	6	2·53
Platinum	1	99	41·49
Nitrogen	1	14	—
Chlorine	3	106·5	44·93
		237·5	

Therefore, the analysed substance is the platinum-salt of methylamine.

The platinum-black used in the preparation of the methylamine was treated with water, and the aqueous solution concentrated on the water-bath. From this concentrated liquid, long prismatic crystals, of a slightly brown colour, separated on its being allowed to stand in the exsiccator. These crystals, easily soluble in water, were the double cyanide of platinum and methylamine, and left a grey residue of platinum on being exposed to a high temperature in air. In order to determine their composition and constitution, their aqueous solution was precipitated with pure chloride of copper, and the green precipitate after careful washing, dried over sulphuric acid.

The filtrate and wash-water of this precipitated substance were united and treated with sulphuretted hydrogen, in order to remove the copper, and the clear supernatant liquid separated from the sulphide of copper and evaporated at 100°C. A colourless, highly hygroscopic residue of hydrochlorate of methylamine was obtained.

The analysis of the precipitate formed by chloride of copper gave the following results:—

0·818 grm. gave, after ignition in air 0·606 grm. residue; this residue, moistened with nitric acid, and again raised to a red heat increased 0·001 grm. in weight. The oxide of copper was extracted from it by diluted nitric acid, and precipitated from this solution by caustic potash. The oxide of copper thus obtained left, after ignition and treatment with hydrochloric acid, 0·005 grm. of silicic acid, most probably derived from the potash. Platinum was not contained in the copper solution. The portion of the residue insoluble in nitric acid was dissolved in aqua regia, and the platinum separated by means of chloride of ammonium and alcohol. The filtrate from the ammonio-chloride of platinum, contained small quantities of copper, which were determined according to the usual method. In this manner 0·430 grm. of platinum and 0·179 grm. of oxide of copper were found.

In 100 parts:

Platinum + oxide of copper	74·20
Platinum	52·5
Copper	17·34

If this compound be regarded as the double cyanide of plati-

num and copper, the following theoretical percentage values are obtained:

Platinum	1	99	54·18
Copper	1	31·7	17·35
Cyanogen	2	52·0	—
		182·7	
Platinum + oxide of copper		.. ..	75·91

A closer agreement between the experimental and theoretical numbers could scarcely be expected, because the analysed body was obtained as a very bulky precipitate, difficult to free by washing from the impurities attaching to it. However, the agreement is close enough to leave no doubt about the nature of the body. The composition is expressed by the formula—

$$Pt\ Cu\ Cy_2$$

The hydrochlorate of methylamine obtained from the filtrate of the cyanide of platinum and copper, was combined with bichloride of platinum. The compound thus formed presented itself in six-sided plates, which were dried in vacuo over sulphuric acid.

0·2646 grm. gave 0·1096 grm. platinum.

Therefore, in 100 parts—

		Calculated according to $CH_5N.HCl + PtCl_2$
Platinum	41·42	41·49

Consequently, the substance is the platinum-salt of the hydrochlorate of methylamine.

The reaction between hydrocyanic acid, hydrogen, and platinum may thus be explained; prussic acid and hydrogen unite and form methylamine:

$$\underbrace{CNH}_{\text{Prussic acid}} + H_4 = \underbrace{CH_5N}_{\text{Methylamine}}$$

which methylamine immediately forms hydrocyanate of methylamine. A portion of the latter is carried off by the hydrogen current, whereas another portion acts on the platinum and forms Pt. $[CH_6N]\ Cy_2$.

$$Pt + HCy + N\left\{\begin{matrix}CH_3\\H_2\end{matrix}\right. HCy = N\left\{\begin{matrix}CH_3\\H_2\end{matrix}\right. HCy.\ Pt\ Cy + H.$$

The double cyanide of methylamine and platinum surrounds the

particles of the platinum-black, and after a sufficient quantity of it has accumulated, prevents the further action of the platinum altogether. If the formation of this platinum-compound did not take place, or could be prevented, then there is no doubt that the method of preparing methylamine, described in the foregoing pages, would be the most ready and convenient mode of procuring this valuable base.

Ammonia, as is well known, becomes converted into cyanide of ammonium during its passage over red-hot charcoal. Kuhlmann* affirms that, besides cyanide of ammonium, marsh-gas is produced. However, under the conditions named, hydrocyanate of methylamine might be formed, for,

$$C_2 + 2NH_3 = N \left\{ \begin{matrix} CH_3 \\ H_2, \end{matrix} \right. HCy.$$

In order to test the latter equation, I induced Mr. Walter Flight to pass a mixture of dry hydrogen and ammonia over small pieces of red-hot charcoal. The gases and vapours passed first through an empty bottle, and after that through a U-tube filled with hydrochloric acid and pieces of glass. In the empty bottle a white crystalline body, most probably cyanide of ammonium collected, because its solution in water smelt like hydrocyanic acid. This crystalline body, and the acid in the U tube, were united and examined by Mr. Flight, according to the known method, for methylamine. He obtained a small quantity of platinum-salt, which should have contained methylamine, if any had been formed in the process. The shape of the crystals, as well as a platinum-determination, showed it to be ammonio-chloride of platinum.

0·1105 grm. gave 0·0494 grm. platinum, or 44·70 p.c.

The ammonio-chloride of platinum contains 44·2 p.c. platinum. A second experiment gave the same results. Therefore it appears that the action of red-hot charcoal on ammonia must be represented by Kuhlmann's equation:

$$C_3 + 4\,NH_3 = 2(NH_3.CNH) + CH_4$$

Binoxide of nitrogen, when passed in company with hydrogen over platinum-black, forms water and ammonia. The question therefore presents itself: would hydrogen and nitrite

* Gmelin's Handbook, translated by Watts, vii., 382. Ann. Chem. and Ch. Pharm. xxxviii, 62.

of ethyl in contact with platinum-black, form water and ethylamine?

Hydrogen was passed through nitrite of ethyl and then over finely divided platinum. A violent action commenced already at ordinary temperatures, the platinum became hot, and the apparatus filled with white clouds. As in the experiments with prussic acid, the tube with the platinum was immersed in a paraffin bath heated to 110° C. and the gases and vapours conducted ultimately through diluted hydrochloric acid. The acid, evaporated at the conclusion of the experiment, left a white crystalline residue having the appearance of chloride of ammonium. Boiling alcohol dissolved a portion of this residue, and this dissolved quantity was combined with bichloride of platinum. The platinum-salt thus obtained contained 43·8 p.c. of platinum, and was consequently ammonio-chloride of platinum. This result agrees with the physical properties exhibited by the small portion of the residue dissolved by alcohol. It was not hygroscopic, did not melt below 100° C., sublimed without residue, and crystallised from water like chloride of ammonium.

The action of hydrogen on nitrite of ethyl in presence of platinum-black may be expressed by the equation:—

$$\left.\begin{matrix} C_2H_5 \\ NO \end{matrix}\right\}O + H_6 = \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\}O + NH_3 + H_2O$$

Mendius has converted prussic acid into methylamine, cyanide of methyl into ethylamine, cyanide of ethyl into propylamine, &c. These interesting reactions are more calculated than any other facts, to afford an insight into the structure of the members of the series $C_n H_{2n+1}$ and therefore deserve a more special consideration than they seem to have hitherto obtained.

If we compare the formulæ of prussic acid and methylamine, it is at once apparent that the carbon of the first combines directly with three atoms of hydrogen, and forms the radicle methyl, which, in conjunction with two atoms of hydrogen and the triatomic nitrogen, forms methylamine:

$$\underbrace{N.CH}_{\text{Prusic acid.}} + H_4 = N \left\{\begin{matrix} CH_3 \\ H_2 \end{matrix}\right. \quad \text{Methylamine.}$$

In an analogous manner, we represent cyanide of methyl by the formula N.C [CH_3]. And because it is converted into ethylamine under the same conditions under which prussic acid is

converted into methylamine, we must conceive the formation of ethylamine in the same manner as that of methylamine. If we adopt for methyl the symbol Me, we have:—

$$\underbrace{\text{N.CMe}}_{\text{Cyanide of methyl}} + \text{H}_4 = \underbrace{\text{N}\left\{\begin{matrix}\text{CMeH}_2\\ \text{H}_2\end{matrix}\right.}_{\text{Ethylamine}}$$

and the same reasoning holds good for all the other nitriles.

$$\text{CMeH}_2 = \text{E}$$

$$\underbrace{\text{N.CE}}_{\text{Cyanide of ethyl.}} + \text{H}_4 = \underbrace{\text{N}\left\{\begin{matrix}\text{CEH}_2\\ \text{H}_2\end{matrix}\right.}_{\text{Propylamine.}}$$

$$\text{C.EH}_2 = \text{Pr}$$

$$\underbrace{\text{N.CPr}}_{\text{Cyanide of propyl.}} + \text{H}_4 = \underbrace{\text{N}\left\{\begin{matrix}\text{CPrH}_2\\ \text{H}_2\end{matrix}\right.}_{\text{Butylamine.}}$$

&c., &c., &c.

The radicles of the alcohols are accordingly represented by the following formulæ:—

$$\begin{aligned}\text{C.H.}\ \text{H}_2 &= \text{Methyl} = \text{Me}\\ \text{C.Me.H}_2 &= \text{Ethyl} = \text{E}\\ \text{C.E.}\ \text{H}_2 &= \text{Propyl} = \text{Pr}\\ \text{C.Pr.}\ \text{H}_2 &= \text{Butyl} = \text{Bu}\\ &\text{\&c., \&c.}\end{aligned}$$

Similar views of the constitution of the alcohol-radicles have been formed at different times, but facts have been hitherto wanting to place the connection of these bodies in such bold relief, as the experiments of Mendius do.

It was well-known that the higher members of the series $\text{C}_n\text{H}_{2n}\text{O}_2$, stearic acid for example, lose by oxidation the group CH_2 once or more times; and that, in this manner, the members of the series $\text{C}_n\text{H}_{2n}\text{O}_2$ and $\text{C}_n\text{H}_{2n-2}\text{O}_4$ may be produced. Kolbe's experiments had shown that acetate and valerate of potash yield, under the influence of the voltaic current, the one carbonic acid and methyl, and the other carbonic acid and butyl. However the knowledge of these facts did not convey that clear insight into the structure of the alcohol-radicles, which is obtained by the synthesis of the bases from hydrogen and the nitriles.

If the symbols Me, E, Pr, and Bu be eliminated in the above formulæ, and CH_3 substituted for Me, and $\text{C}\left\{\begin{matrix}\text{CH}_3\\ \text{H}_2\end{matrix}\right.$ for E, &c., &c.,

it becomes clear, that a radicle higher up in the series, is formed from the next lower one by the substitution of the latter for one atom of hydrogen in methyl. It is perceived that all these radicles are formed by a successive addition of CH_2 to methyl, that all are formed on the type methyl, and their derivatives on the type of the corresponding methyl-derivatives. The long known analogy between the different alcohols is thus established on a solid foundation.

If we adopt the formula $C\begin{cases}Me\\H_2\\HO\end{cases}$ for ethylic alcohol, then we obtain for acetic acid the expression $C\begin{cases}Me\\O\\HO,\end{cases}$ which agrees essentially with Kolbe's and Frankland's views.* The beautiful experiments of these chemists on the decomposition of the nitriles by caustic potash, as well as the formation of cyanide of methyl from acetate of ammonia by Dumas, support this formula.

Three other observations require to be mentioned here:—

By the electrolytic decomposition of acetate of potash, Kolbe obtained methyl, hydrogen and carbonate of potash; by heating a mixture of acetate of potash and soda-lime, Dumas produced marsh-gas and carbonate of potash; and finally Wanklyn, from sodium-methyl and carbonic acid, obtained acetate of soda. The last reaction forms the counterpart to the two former.

The formula $C\begin{cases}Me\\O\\HO\end{cases}$ brings all these facts into a natural connection. The relations of the other alcohols and their derivatives may likewise be expressed by similar formulæ.

$C\begin{cases}H\\H\\H\\H\end{cases}$ = Marsh-gas $\quad C\begin{cases}Me\\H\\H\\H\end{cases}$ = Hydride of ethyl

$C\begin{cases}H\\H_2\\HO\end{cases}$ = Methylic alcohol $\quad C\begin{cases}Me\\H_2\\HO\end{cases}$ = Ethylic alcohol

* Ann. Ch. Pharm., cxiii., 303. Chem. Soc. Qu. J., xiii., 231.

$C\begin{cases}H\\HO\end{cases}$ or $C\begin{cases}H\\H\\O\end{cases}$ Aldehyde of methylic alcohol $C\begin{cases}Me\\HO\end{cases}$ or $C\begin{cases}Me\\H\\O\end{cases}$ = Aldehyde of ethylic alcohol

$C\begin{cases}H\\O\\HO\end{cases}$ = Formic acid $C\begin{cases}Me\\O\\HO\end{cases}$ = Acetic acid

$C\begin{cases}H\\N\end{cases}$ = Prussic acid $C\begin{cases}Me\\N\end{cases}$ = Cyanide of methyl.

These formulæ must be carefully distinguished from Gerhardt's and Williamson's types. In chemistry, as in every other science, the classification of the material forms an essential part. Any classification which is founded on qualitative distinctions only is not scientific; to be so, the principles on which the systematic arrangement of chemical bodies is made to depend, must be obtained from quantitative relations. Solubility, volatility, fusibility, and taste, could not now, as they did 100 years ago, serve as distinguishing signs of a salt, because our knowledge of salts has considerably increased. In other cases, we still follow the example of the old chemists; horny matter, colouring matter, resins, &c., &c., are general terms which remind one of external impressions. Even such definitions of salts as the following,—a salt is the compound of an acid and a base,—are, strictly considered, not very satisfactory; for in one case, a body comports itself like an acid, and in another case like a base, and hence arises a certain confusion in the classification of its compounds.

Gerhardt's and Williamson's types are founded on certain numerical relations, and this circumstance forms their scientific basis. If it be true that chemical reactions form the foundation of all chemical classification, then it follows that reactions themselves must be divided into classes, and different kinds of reactions cannot be used indiscriminately. It is clear that addition of hydrogen to a chemical compound, is a process very different from double decomposition, and both cannot be employed in the same manner in theoretical considerations. Additions and subtractions of elements, or groups of elements, change the structure of a molecule. Under certain conditions, propionic acid may be converted into lactic acid, and the latter, under other conditions, into the former. These known processes do not teach us anything about the chemical relations of propionic and lactic acid, as long as the structure of the molecules of these bodies remains the same,

but exhibit the relation of two different classes of acids to each other. By means of double decomposition, we take a portion of a molecule away and immediately fill the space which thus becomes vacant, by an equivalent quantity of another radical. This process does not alter the structure of a molecule. Now, taking certain conditions into consideration, the question is: Which and how many of the elements of a body may be exchanged by double decomposition?

The formula of acetic acid $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$ expresses that acetic acid belongs to the type water, that the group C_2H_3O, and the elements H and O, may be exchanged for equivalent quantities of other radicles. The numerous derivatives thus obtained from acetic acid still belong to the type water, their molecules are built up in the same manner as those of acetic acid, and the latter may be regenerated from them by a process of simple substitution. If, however, acetic acid be converted into glycollic acid, a molecule of quite another class is obtained; acetic acid, as modern chemistry expresses the fact, is monoatomic; glycollic acid biatomic. Double decomposition, therefore, is the means which Gerhardt recommends for discovering the chemical constitution of bodies, whilst other reactions serve to disclose the relations between different classes of bodies.

The principle of Gerhardt's types may be represented by the question: *"Which and how many parts of a molecule may be exchanged by means of double decomposition, and what are the equivalent values of these parts in comparison with hydrogen?*

A body belonging to the type hydrogen is composed of two monatomic pieces or radicles, which, under certain conditions, may be exchanged for other elements or group of elements.

A body belonging to the type water is supposed to be composed of three parts, two monoatomic, and one biatomic. Under certain conditions, these parts may be exchanged for other radicles of the same chemical value. If we take, as an example, common alcohol, then the formula $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ says: three parts must be distinguished in alcohol, the group C_2H_5 and the elements H and O, the hydrogen being exchangeable for metals, oxygen for sulphur, and ethyl for hydrogen, &c.

A substance composed of one triatomic and three monoatomic radicles, is said to belong to the type ammonia, &c., &c.

Many other types, besides those named, may be formed.

The principle of these types therefore is, *the* COUNTING *of the parts or radicles, which may be distinguished in a body by means of the process of double decomposition, and the determination of the equivalent value of these parts in comparison with hydrogen.* Two bodies which are found by the method just explained, to be composed of the same number of radicles and corresponding atomic value, are said to belong to the same type. These are the numerical relations which form the scientific basis of Gerhardt's types, and constitute their superiority over other methods of classification.

From this point of view a body may belong to different types, or may have more than one rational formula; because, if the conditions be changed under which it takes part in double decompositions, the order in which its elements are exchanged may be entirely altered.* Those chemists who allow only one rational formula for a body, must be struck by the fact, that different well-informed scientific men, do not always adopt the same rational formula for the same substance, but that sometimes, within a short period of time, as many as ten rational formulæ have been introduced for the same body. When several investigators differ very much in their views of a simple case, either the method employed must be at fault, or the knowledge sought for unattainable. If a rational formula is to express the *real arrangement* of the atoms of a body, a little reflection will show the chemical way not to be the true guide to this desirable information.

The foregoing remarks explain the difference between the formulæ $C\begin{cases}Me\\H_2\\HO,\end{cases}$ $C\begin{cases}Me\\O\\HO,\end{cases}$ and the typical expressions formed on the principles of Gerhardt: the first represent different kinds of reactions, the latter only double decompositions. The formation of acetic acid from cyanide of methyl, or from carbonic acid and sodium-methyl, the conversion of acetate of ammonia into cyanide of methyl, and of acetate of potash into carbonate of potash and marsh-gas, are not double decompositions in the ordinary sense of the term. If the composition of acetic acid be represented by the formula $C\begin{cases}Me\\O\\HO,\end{cases}$ then these different reactions are brought into

* Gerhardt, Traité, iv, 576.

natural connection, and in this consists the advantage of this formula. Its foundation, however, is different from that of acetamide and diacetamide.

But, as the scientific comparison of all natural and artificial bodies forms a great branch of the business of the chemical investigator, such distinctions, as mentioned here, are not only useful, but necessary for the development of chemistry.

XXXII.—*On the conversion of Pyroracemic Acid into Lactic Acid.*

By Henry Debus, F.R.S.

Pyroracemic acid is, according to composition, homologous with glyoxylic acid; and although, according to Finck's experiments, it is not decomposed by the hydrate of barium quite in the same manner as glyoxylic acid, yet a general resemblance of both acids in this respect may be recognised. It became, therefore, a matter of interest to institute a comparison between the properties of glyoxylic and pyroracemic acids, in order to obtain a clearer conception of their chemical relations. I have pointed out, on another occasion, that glyoxylic acid dissolves zinc, and becomes converted into glycollic acid.* If pyroracemic acid comports itself with zinc as glyoxylic acid does, lactate of zinc ought to be obtained:

$$2(C_3H_4O_3) + 2Zn = \underset{\text{Pyroracemate of zinc.}}{C_3H_3ZnO_3} + \underset{\text{Lactate of zinc.}}{C_3H_5ZnO_3}$$

Pyroracemic acid dissolves zinc, and produces lactate of zinc, or a salt of the same composition. This fact I had established nearly six months ago, and I intended to publish the results of my experiments together with other researches on pyroracemic acid. However, perceiving by a memoir published in Liebig's Annalen† that Wislicenus is engaged in researches on pyroracemic acid, I am induced to publish the results of my experiments.

* Proceedings of the Royal Society, xii, 429.

† Ann. Ch. Pharm. cxxvi, 225.

The acid liquid obtained in the destructive distillation of tartaric acid was rectified, and the portions, distilling to 130° C, from 130° to 160°, and from 160° to 170° C, collected separately. From each of these distillates lactic acid may be prepared by the following method.

The quantity which distilled from 130° to 160° C, consisting of acetic and pyroracemic acids, was mixed with from two to three times its volume of water, and pieces of zinc introduced into it. The acid acted at once on the metal, and the liquid became perceptibly warm, but the quantity of hydrogen disengaged was less than one would have expected from these appearances. After some time, when the action appeared less brisk, the vessel, with its contents, was exposed to a temperature of 100° C., until the disengagement of hydrogen had almost ceased, and the acid reaction of the liquid nearly disappeared. The whole was now allowed to stand a day or two at ordinary temperatures, then diluted with water, and freed from a white gelatinous mass and metallic zinc by filtration. Through the filtrate a current of sulphuretted hydrogen was allowed to pass, in order to precipitate the zinc, and the liquid, after the removal of the sulphide of zinc, evaporated on the water-bath to the consistency of a syrup. The residue proved to be a strong acid. After dilution with water, small pieces of marble were by degrees put into the liquid, until the disengagement of carbonic acid ceased. Hot absolute alcohol precipitated from this solution a lime-salt, which dissolved readily in water, but could only in one case be obtained in crystals from this solution; in two other preparations, after suitable concentration, a syrup-like mass remained at last, which did not show any signs of crystallisation even after long standing.

In order to obtain the lime-salt from the alcoholic solution, the latter was placed in a distilling apparatus, and the alcohol distilled off. The remaining liquid, exposed to the air, deposited small groups of needle-like crystals, presenting the appearance of lactate of lime.

This substance, after two crystallisations, was pure enough for analysis.

0·923 grm. dried at ordinary temperature in the exsiccator, lost at 118° C 0·269 grm. of water.

0·186 grm. of the anhydrous salt gave 0·084 grm. carbonate of lime.

0·2625 grm. of the anhydrous salt burnt with chromate of lead, gave 0·1055 grm. water.*

According to the above numbers, 100 parts of the crystallised salt contained 29·1 p. c. water; the formula $C_3H_5CaO_3 + 2\frac{1}{2} H_2O$ requires 29·2 p. c. of water.

100 parts of the anhydrous salt contain, according to theory and experiment:—

Carbon.....	3	36	33·0	—
Hydrogen	5	5	4·5	4·46
Calcium	1	20	18·3	18·06
Oxygen	3	48	—	—
		109		

The analysed salt, therefore, agrees in form and composition with lactate of lime, but I am not able to decide, at the present moment, whether the acid of this body is identical, or only isomeric with ordinary lactic acid. Lime-water, bichloride of mercury, acetate of zinc, nitrate of silver, chloride of copper, and nitrate of lead, do not precipitate the diluted solution of the lactate of lime prepared from pyroracemic acid. At higher temperatures, it comports itself like the ordinary lactate of lime, but it does not appear to possess the same degree of solubility in water as the latter. A solution, saturated at 80° C, with the lactate of lime prepared from pyroracemic acid, was allowed to stand in contact with some solid salt, for five or six days, at ordinary temperatures, and now and then the whole well shaken. 2·176 grms. solution, prepared in this manner, left, after the evaporation of the water at 100° C, 0·097 grm. anhydrous salt. Therefore, one part of the crystallised compound requires 14·8 parts of water at 21° C for solution. According to the Handbooks on Chemistry, one part of the lactate of lime prepared from the acid obtained by fermentation, requires 9·5 parts of cold water for its solution. Further experiments are therefore required in order to decide whether the acid from pyroracemic acid is identical or isomeric with ordinary lactic acid.

The action of zinc on a mixture of acetic and pyroracemic acids may take place according to the equation:—

* The carbon determination was lost.

$$\underset{\text{Acetic acid.}}{2C_2H_4O_2} + Zn_2 + \underset{\text{Pyroracemic acid.}}{C_3H_4O_3} = \underset{\text{Acetate of zinc.}}{2C_2H_3ZnO_2} + \underset{\text{Lactic acid.}}{C_3H_6O_3}$$

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} + Zn = \underset{\text{Lactate of zinc.}}{C_3H_5ZnO_3} + H.$$

There are two other acids closely connected with pyroracemic acid, viz. malonic and tartronic acids. Both may be derived from the same source; the malonic acid is formed by the slow oxidation of malic acid, and the tartronic acid by a similar process from tartaric acid, both according to the same equation :—

$$\underset{\text{Malic acid.}}{C_4H_6O_5} - CH_2O = \underset{\text{Malonic acid.}}{C_3H_4O_4}$$

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} - CH_2O = \underset{\text{Tartronic acid.}}{C_3H_4O_5}$$

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} - CH_2O_3 = \underset{\text{Pyroracemic acid.}}{C_3H_4O_3}.$$

Because glyoxylic and pyroracemic acids comport themselves alike with hydrogen in the nascent state, the one forming glycollic and the other lactic acid, both may be considered to be homologous. Pyroracemic acid would then stand to malonic acid as glyoxylic to oxalic acid, whilst the member corresponding to tartronic acid is wanting in the ethyl series, and, most probably, does not exist.

I have to thank my friend, Dr. Atkinson, for the pyroracemic acid used in these experiments.

XXXIII.—*On some Effects of Heat on Fluids.*

By W. R. Grove, Esq., Q.C., F.R.S., &c.

[A Lecture delivered before the Chemical Society, May 21st, 1863.]

Having been honored by an invitation from the Council of the Chemical Society to give a lecture on one of the evening meetings of the Society, it was not without hesitation that I accepted the task. My professional occupation having of late years so much prevented any continuous devotion of mind to scientific investigation, it was only by reverting to researches made several years ago that

there was a chance of my communicating anything worthy the attention of the Society. I had, however, at one period made a rather careful investigation into some phenomena, suggested partly by a paper of M. Donny's, published in 1843, and partly by own experiments on the decomposition of water by heat; and although this investigation did not lead to results as important as were at the time anticipated, yet, as they seemed to add something to our stock of knowledge, and may, it is hoped, form a starting point for important discoveries, I have ventured to bring them forward on this occasion.

The paper of M. Donny (Mémoires de l'Académie Royale de Bruxelles, 1843) makes known the fact that in proportion as water is deprived of air, the character of its ebullition changes, becoming more and more abrupt, and boiling like sulphuric acid with *soubresauts*, and that between each burst of vapour the water reaches a temperature above its boiling point. To effect this, it is necessary that the water be boiled in a tube with a narrow orifice, through which the vapour issues; if it be boiled in an open vessel, it continually re-absorbs air and boils in the ordinary way.

In my experiments on the decomposition of water by heat, I found that with the oxy-hydrogen gas given off from ignited platinum plunged into water, there was always a greater or less quantity of nitrogen mixed; this I could never entirely get rid of, and I was thus led into a more careful examination of the phenomenon of boiling water, and set before myself this problem—what will be the effect of heat on water perfectly deprived of air or gas?

Two copper wires were placed parallel to each other through the neck of a Florence flask, so as nearly to touch the bottom, joining the lower ends of these was a fine platinum wire, about $1\frac{1}{2}$ inch long, and bent horizontally into a curve. Distilled water which had been well boiled, and cooled under the receiver of an air-pump, was poured into this flask so as to fill about one-fourth of its capacity. It was then placed under the receiver of an air-pump, and one of the copper wires brought in contact with a metallic plate covering the receiver, the other bent backwards over the neck of the flask, and its end made to rest on the pump plate. By this means, when the terminal wires from a voltaic battery were made to touch, the one the upper and the other the lower plate, the platinum wire would be heated, and the boiling continued indefinitely in the vacuum of a very excellent air pump. The effect was very curious; the water did not boil, but at inter-

vals a burst of vapour took place, dashing the water against the sides of the flask, some escaping into the receiver. (There was a projection at the central orifice of the pump plate to prevent this overflow getting into the exhausting tube.)

After each sudden burst of vapour, the water became perfectly tranquil, without a symptom of ebullition until the next burst took place. These sudden bursts occurred at measured intervals, so nearly equal in time that, had it not been for the escape from the flask, at each burst, of a certain portion of water, the apparatus might have served as a timepiece.

I showed this experiment at one of my lectures at the time, as affording an illustration of the action of the geysers, of which it seemed to me to afford a rational explanation. Supposing a source of heat at a certain depth beneath the earth's surface, and subterranean wells whose only communication with the air was a narrow tube, probably formed by the issue of vapour, the air, if any, dissolved in the water of these wells would be expelled, and the boiling would take place at intervals and by sudden bursts instead of in the ordinary way.

This experiment, though instructive, did not definitively answer the question I had proposed, as I could not of course ascertain whether there was some minute residuum of gas which would form the nucleus for each ebullition, and I proceeded with others. A tube of glass, 5 feet long, and $\frac{4}{10}$ths inch internal diameter, was bent into a V shape, into one end a loop of platinum wire was hermetically sealed with great care, and the portion of it in the interior of the tube was platinized. When the tube had been well washed, distilled water, which had been purged of air as before, was poured into it to the depth of 8 inches, and the rest of the tube filled with olive oil; when the V was inverted, the open end of the tube was placed in a vessel of olive oil, so that there would be 8 inches of water resting on the platinum wire, separated from the external air by a column of 4 feet 4 inches of oil. The projecting extremities of the platinum wire were now connected with the terminals of a voltaic battery and the water heated; some air was freed and ascended to the level of the tube—this was made to escape by carefully inverting the tube so as not to let the oil mix with the water, and the experiment continued. After a certain time the boiling assumed an uniform character, not by such sudden bursts as in the Florence flask experiment, but with larger and more distinct bursts of ebullition than in its first boiling.

The object of platinizing the wire was to present more points for the ebullition, and to prevent *soubresauts* as much as possible.

The experiment was continued for many hours, and in some repetitions of it for days. After the boiling had assumed an uniform character, the progress of the vapour was carefully watched, and as each burst of vapour condensed in the oil, which was kept cool, it left a minute bead of gas, which ascended through the oil to the bend of the tube: a bubble was formed here which did not seem at all absorbed by the oil. This was analysed by a eudiometer, which I will presently describe, and proved to be nitrogen. The beads of gas, when viewed through a lens and micrometer scale at the same height in the tube, appeared as nearly as may be of the same size. No bubble of vapour was condensed completely, or without leaving this residual bubble. The experiment was frequently repeated, and continued until the water was so nearly boiled away, that the oil, when disturbed by the boiling, nearly touched the platinum wire; here it was necessarily stopped.

To avoid any question about the boiling being by electrical means, similar experiments were made with a tube, without a platinum wire, closed at its extremity, and the boiling was produced by a spirit lamp. The effects were the same, but the experiment was more difficult and imperfect, as the bursts of vapour were more sudden, and the duration of the intervals more irregular.

The beads of gas were extremely minute, just visible to the naked eye. I cannot find any record of their exact measure.

In these experiments there was no pure boiling of water, *i.e.*, no rupture of cohesion of the molecules of water itself, but the water was boiled, to use M. Donny's expression, by evaporation against a surface of gas.

It is hardly conceivable that air could penetrate through such a column of oil, the more so as the oil did not perceptibly absorb the nitrogen freed by the boiling water and resting in the bend of the tube; but to meet this conjectural difficulty, the following experiment was made. A tube, one foot long and $\frac{2}{10}$ths inch internal diameter, bent into a slight angle, had a bulb of $\frac{3}{4}$ inch diameter blown on it at the angle; this angle was about 3 inches from one end and 9 from the other; a loop of platinum wire was sealed into the shorter leg, and the whole tube and bulb filled with and immersed into mercury; water, distilled and purged of air as before, was allowed to fill the short leg, and by carefully adjusting

the inclination, the water could be boiled so as to allow bubbles to ascend into the bulb and displace the mercury. The effect was the same as with the oil experiment, no ebullition without leaving a bead of gas, the gas collected in the bulb, and was cut off by what may be termed a valve of mercury, from the boiling water, then allowed to escape, and so on; the experiment was continued for many days, and the bubbles analyzed from time to time; they proved, as before, to be nitrogen, and, as before, continued indefinitely.

A similar experiment was made without the platinum wire, and though, from the greater difficulties, the experiment was not so satisfactory, the result was the same.

As the mercury of the common barometer will keep air out of its vacuum for years, if not for centuries, there could be no absorption here from the external atmosphere, and I think I am fairly entitled to conclude from the above experiments,—which I believe went far beyond any that have been recorded,—that no one has yet seen the phenomenon of pure water boiling, *i.e.*, of the disruption of the liquid particles of the oxy-hydrogen compound so as to produce vapour which will, when condensed, become water, leaving no permanent gas. Possibly, in my experiment of the decomposition of water by ignited platinum, it may be that the sudden application of intense heat, and in some quantity, so forces asunder the molecules that, not having sufficient nitrogen dissolved to supply them with a nucleus for evaporation, the integral molecules are severed, and decomposition takes place. If this be so, and it seems to me by no means a far-fetched theory, there is probably no such thing as boiling, properly so called, and the effect of heat on liquids in which there is no dissolved gas may be to decompose them.

Considerations such as these led me to try the effect of boiling on an elementary liquid, and bromine occurred as the most promising one to work upon; as bromine could not be boiled in contact with water, oil, or mercury, the following plan was ultimately devised. A tube, 4 feet long and $\frac{4}{10}$ths inch diameter, had a platinum loop sealed into one closed extremity; bromine was poured into the tube to the height of 4 inches; the open end of the tube was then drawn out to a fine point by the blow-pipe, leaving a small orifice; the bromine was then heated by a spirit lamp; and when all the air was expelled, and a jet of bromine vapour issued from the point of the tube, it was sealed by the blow-pipe. There was then, when the bromine vapour had condensed, a vacuum in the

tube above the bromine. The platinum loop was now heated by a voltaic battery and the bromine boiled: this was continued for some time, care being taken that the boiling should not be too violent. At the end of a certain period—from half-an-hour to an hour—the platinum loop gave way, being corroded by the bromine; the quantity of this had slightly decreased. On breaking off, under water, the point of the tube, the water mounted and showed a notable quantity of permanent gas, which on analysis proved to be pure oxygen. As much as a quarter of a cubic inch was collected at one experiment. The platinum wire, which had severed at the middle, was covered with a slight black crust, which, suspecting to be carbon, I ignited by a voltaic spark in oxygen in a small tube over lime water; it seemed to give a slight opalescence to the liquid, but the quantity was so small that the experiment was not to be relied on. No definite change was perceptible in the bromine; it seemed to be a little darker in colour and had a few black specks floating in it, which I judged to be minute portions of the same crust which had formed on the platinum wire, and which had become detached.

The experiment was repeated with chloride of iodine and with the same result, except that the quantity of oxygen was greater; I collected as much as half a cubic inch in some experiments, from an equal quantity of chloride of iodine, the platinum wire, however, was more quickly acted on than with the bromine, and the glass of the tube around it to some extent.

Melted phosphorus was exposed to the heat of the voltaic disruptive discharge by taking this between platinum points in a tube of phosphorus, similarly to an experiment of Davy's, but with better means of experimenting; a considerable quantity of phosphuretted hydrogen was given off, amounting in several experiments to more than a cubic inch.

A similar experiment was made with melted sulphur and sulphuretted hydrogen given off, but not in such quantities as the phosphuretted hydrogen. I tried in vain to carry on these experiments beyond a certain point; the substance became pasty, mixed with platinum from the arc, and from the difficulty of working with the same freedom as when they were fresh, the glass tubes were always broken after a certain time. Had I time for working on the subject now, I should use the discharge from the Rhumkorf coil, which had not been invented at the period of these experiments. At a subsequent period, when this discharge

was taken in the vacuous receiver of an air-pump from a metallic point to a metallic capsule containing phosphorus, a considerable yellow deposit lined the receiver, which, on testing, turned out to be allotropic phosphorus. No gas is, however, given off. I had an air-pump (described, Phil. Trans., 1852, p. 101) which enabled me to detect very small quantities of gas, but I could get none. It was in making these experiments that I first detected the striæ in the electric discharge, which have since become a subject of such interesting observations, which are seen, perhaps, more beautifully in this phosphorus vapour than in any other medium, and which cease, or become very feeble, where the allotropic phosphorus is not produced.

I tried also phosphorus highly heated by a burning glass in an atmosphere of nitrogen, but could eliminate no perceptible quantity of gas, though the phosphorus was changed into the allotropic form.

It is not difficult to understand why gas is not perceptibly eliminated in the last two experiments; the effect is probably similar to that described in my paper on "the Decomposition of Water by Heat," where, when the arc or electric spark is taken in aqueous vapour, a minute bubble of oxyhydrogen gas is freed and disseminated through the vapour, recombination being probably prevented by this dilution; but, however long the experiment may be continued, no increased quantity of the gas is obtained, all beyond this minute quantity being recombined. If, however, the bubble of gas be collected, by allowing the vapour to cool, and then expelled, a fresh portion is decomposed and so on.

So with the phosphorus in the experiments in the air-pump and with the burning glass, if any gas is liberated it is probably immediately recombined with the phosphorus; possibly a minute residuum might escape recombination, but the circumstances of the experiment did not admit of this being collected, as the gas was with the aqueous vapour.

When, on the other hand, the gas freed is immediately cut off from the source of heat, as when the spark is taken in liquids, an indefinite quantity can be obtained.

Decomposition and the elimination of gas may thus take place by the application of intense heat to a point in a liquid, or also in gas or vapours, but in the latter case it is more likely to be masked by the quantity of gas or vapour through which it is disseminated.

I believe there are very few gases in which some alteration does

not take place by the application of the intense heat of the voltaic arc or electric spark. If the arc be taken between platinum points in dry oxygen-gas over mercury, the gas diminishes indefinitely, until the mercury rises, and by reaching the point where the arc takes place, puts an end to the experiment. I have caused as much as a cubic inch of oxygen to disappear by this means. I at one time thought this was due to the oxidation of the platinum, but the high heat renders this improbable, and the deposit formed on the interior of the glass tube in which the experiment is made has all the properties of platinum-black; so if the spark from a Ruhmkorf coil be taken in the vapour of water for several days, a portion of gas is freed which is pure hydrogen, the oxygen freed being probably changed into ozone and combined with the mercury or dissolved by the water.

I have alluded to the eudiometer by which I analysed the gases obtained in these experiments; it was formed simply of a tube of glass frequently not above $2\frac{1}{2}$ millemetres in diameter, with a loop of wire hermetically sealed into one end, the other having an open bell-mouth. By a platinum wire a small bubble of the gas to be examined could be got up through water or mercury into the closed end of the tube, and by the addition of a bubble of oxygen or hydrogen gas, a very accurate analysis of very minute quantities of gas could be made; I have analysed by this means quantities no larger than a partridge-shot.

I need hardly allude to results on the compound liquids such as oils and hydrocarbons, as the fact that permanent gas is given off in boiling such liquids would not be unexpected; but the above experiments seem to show that boiling is by no means necessarily the phenomenon that has generally been supposed, viz. a separation of cohesion in the molecules of a liquid from distension by heat. I believe, from the close investigation I made into the subject, that (except with the metals, on which there is no evidence) no one has seen the phenomenon of pure boiling without permanent gas being freed, and that what is ordinarily termed boiling arises from the extrication of a bubble of permanent gas either by chemical decomposition of the liquid, or by the separation of some gas associated in minute quantity with the liquid, and from which human means have hitherto failed to purge it; this bubble once extricated, the vapour of the liquid expands it, or, to use the appropriate phrase of M. Donny, the liquid evaporates against the surface of the gas.

My experiments are, in a certain sense, the complement of his. He showed that the temperature of the boiling point was raised in some proportion as water was deprived of air, and that under such circumstances the boiling took place by *soubresauts*. I have, I trust, shown that when the vapour liberated by boiling is allowed to condense, it does not altogether collapse into a liquid, but leaves a residual bubble of permanent gas, and that at a certain point this evolution becomes uniform.

Boiling, then, is not the result of merely raising a liquid to a given temperature, it is something much more complex.

One might suppose that with a compound liquid the initial bubble by which evaporation is enabled to take place might, if all foreign gas were or could be extracted, be formed by decomposition of the liquid, but this could not be the case with an elementary liquid; whence the oxygen from bromine or the hydrogen from phosphorus and sulphur? as with the nitrogen in water, it may be that a minute portion of oxygen, hydrogen, or of water is inseparable from these substances, and that if boiled away to absolute dryness, a minute portion of gas would be left for each ebullition.

With water there seems a point at which the temperature of ebullition and the quantity of nitrogen yielded become uniform, though the latter is excessively minute.

The circumstances of the experiments with bromine, phosphorus, and sulphur, did not permit me to push the experiment so far as was done with water, but as far as it went the result was similar.

When an intense heat, such as that from the electric spark or voltaic arc, is applied to permanent gas, there are, in the greater number of cases, signs either of chemical decomposition or of molecular change; thus compound gases, such as hydrocarbons, ammonia, the oxides of nitrogen, and many others are decomposed. Phosphorus in vapour is changed to allotropic phosphorus, oxygen to ozone, which, according to present experience, may be viewed as allotropic oxygen; there may be many cases where, as with aqueous vapour, a small portion only is decomposed, and this may be so masked by the volume of undecomposed gas as to escape detection; if, for instance, the vapour of water were incondensable, the fact that a portion of it is decomposed by the electric spark or ignited platinum would not have been observed.

All these facts show that the effect of intense heat applied to liquids and gases is far more complex, and presents greater

interest to the chemist than has generally been supposed. In far the greater number of cases, possibly in all, it is not mere expansion into vapour which is produced by intense heat, but there is a chemical or molecular change. Had circumstances permitted I should have carried these experiments further and endeavoured to find an *experimentum crucis* on the subject; there are difficulties with such substances as bromine, phosphorus, &c., arising from their action on the substances used to contain and heat them, which are not easy to vanquish, and those who may feel inclined to repeat my experiments will find these difficulties greater than they appear in narration; but I do not think they are insuperable, and hope that, in the hands of those who are fortunate enough to have time at their disposal, they may be overcome.

To completely isolate a substance from the surrounding air and yet be able to experiment on it, is far more difficult than is generally supposed. The air-pump is but a rude mode for such experiments as are here detailed.

Caoutchouc joints are out of the question; even platinum wires carefully sealed into glass, though, as far as I have been able to observe, forming a joint which will not allow gas to pass, yet it is one through which liquids will effect a passage, at all events when the wires are repeatedly heated.

In some experiments with the ignited platinum wire hermetically sealed into a tube of glass, the end of the tube containing the platinum wire was placed in a larger tube of oil to lessen the risk of cracking the glass. After some days experimenting, though the sealing remained perfect, a slight portion of carbon was found in the interior liquid. This does not affect the results of my experiments, as I repeated them with glass tubes closed at the end and without platinum wires, and also without the oil-bath, but it shows how difficult it is to exclude sources of error. When water has been deprived of air to the greatest practicable extent it becomes very avid for air. The following experiment is an instance of this: A single pair of the gas-battery, the liquid in which was cut off from the external air by a greased glass stopper, having one tube filled with water, the other with hydrogen, the platinized platinum plates in each of these tubes were connected with a galvanometer, and a deflection took place from the reaction of the hydrogen on the air dissolved in the water. After a time the deflection abated, and the needle returned to zero, all the oxygen of the air having become combined with the hydrogen. If now

the stopper were taken out, a deflection of the galvanometric needle immediately took place, showing that the air rapidly enters the water as water would a sponge. Absolute chemical purity in the ingredients is a matter, for refined experiments, almost unattainable; the more delicate the test, the more some minute residual product is detected; it would seem (to put the proposition in a somewhat exaggerated form) that in nature everything is to be found in anything if we carefully look for it.

I have indicated the above sources of error to show the close pursuit that is necessary when looking for these minute residual phenomena. Enough has, I trust, been shown in the above experiments to lead to the conclusion that, hitherto, simple boiling, in the sense of a liquid being expanded by heat into its vapour without being decomposed or having permanent gas eliminated from it, is a thing unknown. Whether such boiling can take place may be regarded as an open question, though I incline to think it cannot; that if water, for instance, could be absolutely deprived of nitrogen, it would not boil until some portion of it was decomposed; that the physical severance of the molecules by heat is also a chemical severance. If there be anything in this theoretic view, there is great promise of important results on elementary liquids, if the difficulties to which I have alluded can be got over.

The constant appearance of nitrogen in water, when boiled off out of contact with the air almost to the last drop, is a matter well worthy of investigation. I will not speculate on what possible chemical connexion there may be between air and water; the preponderance of these two substances on the surface of our planet, and the probability that nitrogen is not the inert diluent in respiration that is generally supposed, might give rise to not irrational conjectures on some unknown bond between air and water. But it would be rash to announce any theory on such a subject; better to test any guess one may make, by experiment than to mislead by theory without sufficient data, or to lessen the value of facts by connecting them with erroneous hypotheses.

XXXIV.—*On the Constitution of Salts.*

[A Lecture delivered before the Chemical Society, May 7th, 1863.]

By Lyon Playfair, LL.D., F.R.S.

Various views have been taken with regard to the classification of salts, but the chief theories are three in number.

The dualistic view supposes that salts are constituted of bases and acids which have an affinity for each other, owing to their opposite basylous and chlorous characters.

The salt-radicle theory views haloid and oxysalts as being constituted on the same type, the only difference being that, in one case, there are simple halogens, and, in the others, compound halogens, as chlorous constituents.

In consequence of the new system of notation followed by Gerhardt, a third system of classification was introduced and has received the support of many leading chemists. On this system, there are only a few typical bodies necessary for classification, and, under these types, all chemical elements and compounds may be grouped.

The four types are as follow:—

Hydrogen	H.H
Hydrochloric acid	H.Cl
Ammonia	NH_3
Water	H_2O_2.

Besides these types or their multiples, the requirements of the science as it progressed, demanded "mixed types," formed by the coalescence of two distinct types. Undoubtedly the comprehensiveness of this system of types, and the clear account which it gives of the phenomena of decompositions and recompositions, justify the favour which it has received from chemists. But to my own mind it has not carried conviction, at least to the full extent which has been accorded to it by chemists generally; and as it is a useful exercise in our science to look at the constitution of compounds from various points of view, I have ventured to ask your attention this evening to the manner in which I am accustomed to regard the constitution of salts. As we proceed, it will

be seen that, in the construction of my building, I use very freely the materials left in the remains of the venerable dualistic edifice, and I am glad to borrow also the strong and sound cement which Gerhardt and his followers have mixed up for the use of all chemists. Whether this cement will adhere tenaciously to the old materials or not, I do not know, but the strength of the structure is likely to be tried this evening by young and vigorous hands which will speedily disintegrate it if incoherent.

During recent years much attention has been devoted to the atomicities of elementary bodies and their compounds. The sense, however, in which the term atomicity is held varies with different chemists. According to one class of chemists, if nitrogen unites with five atoms of oxygen, it has a pentatomic power in combination, and may replace five equivalents of hydrogen in a compound. In the other sense, nitrogen is pentatomic because it is capable of saturation with five atoms of oxygen or other radicle, but 14 parts of nitrogen still equal 1 part of hydrogen. It is in the latter sense only that I speak of the atomicities of the elements. I need not enlarge upon the tendencies of different elements to acquire a certain number of atoms to reach a stage of repose, or to appropriate an additional number to attain their state of saturation, because this subject has already been fully brought before the Society by Dr. Frankland.* Each element might in fact be said to have as many atomicities as it forms distinct compounds with an increasing number of atoms of any other body, but, in a more limited sense, the atomicities are represented by those stages of repose which it manifests in its way to its highest period of saturation. In the oxides of manganese, for example, we find a distinct period of repose in the peroxide Mn_2O_4, an oxide which enjoys strict neutrality, but which becomes basylous by the removal of oxygen, and chlorous by increments of that element. It is, however, not constant that neutrality is the result of periods of atomic rest.

Thus we have characteristic teroxides, such as those of arsenic, antimony, and nitrogen, when their atoms at least, if not their molecules, enjoy active chemical characters. In all bodies of active chemical habits, there is a want of symmetrical formation, which demands the accession of new atoms to produce that symmetry which is essential for an independent existence. Such

* Frankland—*Organo-metallic Bodies*, Chem. Soc. Qu. J., xiii, p. 227; and Phil. Trans., 1852, p. 438.

bodies as the teroxides, with odd numbers of atoms of oxygen, double themselves into molecules, when this symmetry cannot be attained by union with additional atoms of other bodies. The chemical activity of a body depends upon two circumstances, (1) its want of the conditions of symmetry necessary for a period of repose or of saturation; (2) its greater or less amount of zincous or chlorous elements by which its basylous or chlorous characters are determined. In the oxides of manganese we find that the atoms of the protoxide and sesquioxide, both containing an uneven number of atoms of oxygen, are basylous, being still impressed with the zincous character of the metal; that, in the peroxide, with conditions for symmetry in an even number of atoms of oxygen, there is a strict neutrality; but that an accession of oxygen now impresses its chlorous character upon the oxide, manganic and permanganic acids being strongly chlorous. In bodies with conditions of symmetry, we generally find that the atom and molecule is the same, as in NO_2 and NO_4; while in the compounds which are unsymmetrical, we find the molecule double that of the atom, as in N_2O_2 protoxide of nitrogen; N_2O_6 nitrous acid; N_2O_{10} nitric acid. As the unsymmetrical body shows active properties, which may either be basylous or chlorous according to the relative amount and original character of its constituents, we may expect to find that, even with a fully gratified atomicity, the product may differ in character according to the nature of the combining atoms. We see this fact well illustrated in the organo-metallic bodies, as for example, in arsenious or arsenic acid, where the substitution of basylous methyl for chlorous oxygen gradually overpowers the acid character of the type, until, in the oxide of tetramethylarsonium, we have a base comparable in power with the caustic alkalies. (Frankland.)

In entering upon the constitution of salts, it is necessary that we should understand in what sense I use the term *radicle*. As I understand a radicle, it is the portion of any compound which is moveable under a given set of decompositions and recompositions. Under this definition there may be primary and secondary radicles in the same compound. Thus, in alcohol, we have as a secondary radicle, ethyl C_4H_5, but, by another set of decompositions, we may have ethylene C_4H_4 as the radicle, this body having united with hydrogen to form ethyl in its way to a completed atomicity as presented in hydride of ethyl $C_4H_4H.H = C_4H_6$. In like manner when we act on peroxide of manganese by an oxygen-acid, the

secondary moveable radicle is MnO, the protoxide, but when we act on it by hydrochloric acid the primary radicle is the metal itself—

1. $MnO.O + HO.NO_5 = MnO.NO_5 + HO + O.$
2. $MnO.O + 2HCl = MnCl + 2HO + Cl.$

We admit this view in the case of certain oxides without difficulty. Thus the protoxide of uranium is an admitted radicle in the chloride of uranyl $U_2O_2.Cl$ or in the nitrate $U_2O_2,O.NO_5$. (Peligot.) We admit it also in like compounds with chromium, and see a probability of it in sesquisalts of iron and in aluminous silicates. (Odling's Chemistry, p. 134.)

In examining the series of oxides presented to us by nature, it is therefore not probable that they are all built up from the primary radicle by successive increments of oxygen, but it is more likely that the lower oxides act as radicles to the higher oxides. By this is meant, that in such oxides as peroxide of manganese and manganic acid, the protoxide in the first case and the peroxide in the second, may be the radicles uniting with oxygen.

Peroxide of manganese.. $Mn_2O_2.O_2 = Mn_2O_4$
Manganic acid ..... $Mn_2O_4.O_2 = Mn_2O_6.$

In such cases, we are to expect that the oxygen which unites with the lower oxide may be displaced by other radicles playing its part in the gratified atomicity of the primary radicle. Thus in peroxide of tin, $Sn_2O_2.O_2$ we find the last two atoms of oxygen substituted by ethyl, as in stannic oxydiethide $Sn_2O_2.(C_4H_5)_2$. But when we see these atoms of oxygen substituted by zincous atoms, it cannot be surprising that we should very frequently see them replaced by chlorous atoms chemically analogous to themselves. This is in fact the function of anhydrides, either when they unite directly with oxides to form salts, or by the exchange of water with which they may be already combined. The nature of this substitution may perhaps be better understood if we confine our attention for the present to that class of salts which are known as neutral salts. They are constituted, according to this view, on the type of the neutral peroxides by the replacement of an atom of oxygen by an atom of an anhydride.

Peroxide ..... MO.O or $M_2O_2.O_2$
Neutral salt ..... MO.A or $M_2O_2.A_2$.

It is to be observed that this view has the merit of closely adhering to the analogies of the case. In most neutral salts on this type the condition of neutrality is really achieved, that is, the basylous and the chlorous characters of the constituents have disappeared in the product. This is precisely the case in most peroxides, though not in all of them. On the water type, neutral salts are constructed on the type of oxides of highest basic character, as instanced by soda, oxide of lead, and the protoxides generally. In other words, salts distinguished for their neutrality are built upon a type marked only by active basicity. But in viewing a salt as consisting of MO.A, like MO.O, the peroxide from which it is derived, it is essential to show that an anhydride can displace oxygen, and also that oxygen may displace an anhydride. As an instance of the first reaction, I may quote the decomposition of peroxide of barium by carbonic acid, as described by Duprey, or that of binoxide of sodium as mentioned by Harcourt.

$$Ba_2O_2 . O_2 + C_2O_4 = Ba_2O_2 . C_2O_4 + O_2$$
$$Na_2O_2 . O_2 + C_2O_4 = Na_2O_2 . C_2O_4 + O_2.$$

These equations represent simply the facts of the case without hypothesis; let us compare them in this respect with an equation on the water type—

$$\left.\begin{matrix} Ba'' \\ 2 \end{matrix}\right\} O_4 + \left.\begin{matrix} C_2O_2'' \end{matrix}\right\} O_2 = \left.\begin{matrix} Ba'' \\ C_2O_2'' \end{matrix}\right\} O_4 + O_2.$$

In the latter equation two hypotheses are required, viz., that one atom of barium in the peroxide functions as two atoms of hydrogen, and secondly, that in the carbonate it functions only as one atom of hydrogen.

The converse of this decomposition, where oxygen displaces an anhydride, occurs, though not frequently. It is brought into action in the process for recovering the manganese from its chloride formed in the manufacture of chloride of lime. The first step in this process is, to form a carbonate of manganese; the second, to substitute oxygen for the anhydride by heating it in the air. (Forchammer, Tennent.)

$$Mn_2O_2.C_2O_4 + O_2 = Mn_2O_2.O_2 + C_2O_4.$$

We see like reactions when oxygen replaces carbonic acid in the preparation of minium from white lead, or when acetic acid is displaced by oxygen in the process of ageing mordants for the calico-printers.

It frequently happens that water functions as part of the oxygen in an oxide or of the anhydride in a salt. We see an instance of this in the action of water on tetroxide of potassium. (Harcourt, Chem. Soc. Qu. J., xiv., 267.)

$$KO_2.O_2 + 2HO = KO_2.2HO + O_2.$$

It is true that no definite hydrate of this kind is obtained in a separate state in the case of potassium, although the hydrate of the corresponding binoxide of sodium is described, the reason being that on evaporation the water displaces another atom of oxygen from the binoxide of potassium. The converse takes place, although only partially, when hydrated potash in a state of fusion absorbs oxygen with the displacement of water. (Bloxam, Chem. Soc. Qu. J., xiv, 145.) The reciprocal functions of water, oxygen, and an anhydride may be advantageously compared in their relations to peroxide of barium.

1. $Ba_2O_2.O_2 + 2HO = Ba_2O_2.2HO + O_2$
2. $Ba_2O_2.2HO + 2O = Ba_2O_2.2O + 2HO.$
3. $Ba_2O_2.O_2 + C_2O_4 = Ba_2O_2.C_2O_4 + O_2$
4. $Ba_2O_2.2HO + C_2O_4 = Ba_2O_2.C_2O_4 + 2HO.$

The first and second equations represent Boussingault's plan for preparing oxygen on a large scale, by passing air over hydrate of baryta, and then expelling the oxygen by a jet of steam. In the first case, we observe water taking the place of oxygen; in the second place, oxygen taking the place of water. The third equation represents Duprey's process for making peroxide of hydrogen (Compt. rend., lv. 736), and shows an anhydride expelling and substituting oxygen,—while the fourth equation indicates the familiar action of carbonic anhydride on hydrate of baryta where the acid takes the place of water. As a general result of these equations, we see in the type, $M_2O_2.R_2$, that the position R_2 may be occupied indifferently, either by oxygen, a chlorous anhydride, or by water.* We might quote numerous instances in

* The burning of limestone, during which steam is necessary, is probably a displacement of the anhydride by water at a temperature incompatible with the

which water and anhydrides mutually replace each other; but perhaps one example will suffice (Wurtz).

Glycol.....	$C_4H_4O_2$.	HO,HO
Monacetate of ethylene....	$C_4H_4O_2$.	HO, $(C_4H_3O_3)$
Binacetate of ethylene	$C_4H_4O_2$.	$2(C_4H_3O_3)$.

The acetins of glycerin will also occur as an instance of the case in point. According to the view now taken, peroxides, salts, and their hydrates are analogous :—

Peroxide.....	$M_2O_2.O_2$.
Neutral salts.....	$M_2O_2.A_2$.
Hydrates	$M_2O_2.(aq.)_2$.

It is quite true that anhydrides as such do not manifest any great desire to expel oxygen from a peroxide in order to unite with its radicle the protoxide. But neither does ethyl exercise a strongly basylous character when free. Both the alcohol-radicles and the anhydrides possess unsymmetrical atoms, and double by uniting with themselves into salt-molecules, and as such are comparatively indifferent. In the hydrated acids, however, we have the atom of these chlorous bodies ready to exercise their functions. Hydrated acids of the type to which we are now confining our attention, represent peroxide of hydrogen in which oxygen is replaced by an anhydride.

Peroxide of hydrogen	HO.O.
Hydrated acid	HO.A.
Metallic derivative.....	MO.A.

This is merely symbolising Gerhardt's definition of an acid—namely, "a salt whose basyl is hydrogen." It may here be useful to take two simple cases of decomposition,—the solution of lime in sulphuric acid and the addition of potash to sulphate of zinc, for comparing the constitution of salts on the water type and on the peroxide type.

permanent existence of the hydrate. No doubt the escape of the carbonic anhydride is also facilitated by the presence of a gaseous atmosphere of steam into which it can diffuse.

1. Water type.... $\left.\begin{matrix}H_2\\S_2O_4\end{matrix}\right\}O_4 + Zn_2 = \left.\begin{matrix}Zn_2\\S_2O_4\end{matrix}\right\}O_4 + H_2.$
   Peroxide type.. $H_2O_2.S_2O_6 + Zn_2 = Zn_2O_2.S_2O_6 + H_2.$

2. Water type.... $\left.\begin{matrix}Zn_2\\S_2O_4\end{matrix}\right\}O_4 + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O_2\right) = \left.\begin{matrix}K_2\\S_2O_4\end{matrix}\right\}O_4 + \left.\begin{matrix}Zn_2\\H_2\end{matrix}\right\}O_4$
   Peroxide type.. $Zn_2O_2.S_2O_6 + K_2O_6.2HO = K_2O_2.S_2O_6 + Zn_2O_2.2HO.$

Both views give simple accounts of the transaction, but their differences will be more apparent if we formulate the acid and its salt along with the type:—

	Peroxide type.	Water type.
Type.....	$H_2\left\{\begin{matrix}O_2\\O_2\end{matrix}\right.$	$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4$
Acid.....	$H_2\left\{\begin{matrix}O_2\\S_2O_6\end{matrix}\right.$	$\left.\begin{matrix}H_2\\S_2O_4\end{matrix}\right\}O_4$
Salt	$Zn_2\left\{\begin{matrix}O_2\\S_2O_6\end{matrix}\right.$	$\left.\begin{matrix}Zn_2\\S_2O_4\end{matrix}\right\}O_4$

In the first view the acid, "a salt with its basyl hydrogen," is built upon its type according to strict analogy, a chlorous anhydride substituting its chlorous oxygen, while, in its metallic derivative, the basylous hydrogen is replaced by a basylous metal. On the water type, one portion of the basyl is replaced by a basylous metal, and another portion of the basyl by a chlorous radicle. The advocates of the latter view, however, could point with much propriety to the substitution of all the basylous by the chlorous radicle in the anhydrides as $\left.\begin{matrix}S_2O_4\\S_2O_4\end{matrix}\right\}O_4$. On the peroxide type, anhydrides are simply related to the salts, as may be shown by taking nitric acid as an example—

Peroxide type.....	HO.O
Molecule of protoxide	MO.MO
Nitric anhydride	$(NO_4)O.(NO_4)O$
Nitric acid.....	$HO.(NO_4)O$
Nitrate	$MO.(NO_4.)O$

It may further be contended that in the water type, $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, there is a complete replacement of the basyl radicles, while in the peroxide type, $H\left\{\begin{matrix}O\\O\end{matrix}\right.$ there is only a partial substitution of the oxygen. But this objection could only arise from a misconception of the type, as the whole argument implies that it

should be written MO.O, the protoxide acting as a radicle. In hydride of ethyl, $C_4H_5.H$, we expect to replace one part of the hydrogen as we do in chloride of ethyl $C_4H_5.Cl$, but the fifth atom of hydrogen in ethyl is persistent in many recompositions, although it may at last be removed as in chloride of ethylene, $C_4H_4.Cl_2$. Ethylene here may be viewed as the primary radicle, like the metal in the peroxide, while ethyl represents the secondary radicle, the protoxide. In point of fact we do occasionally find the primary radicle assuming anhydrides directly instead of oxygen, as in the following cases, where, for simplicity of expression, we write the hydrocarbon and oxidised olefines by symbols and sulphuric anhydride, S_2O_6, by the symbol A_2 :—

Ethylene....	$(C_4H_2H_2)$	= E
Othylene....	$(C_4H_2O_2)$	= Ot.

The compounds are either on the type of glycol or of diethelenic-glycol :—

Glycol.....	$EO_2.2HO$
Isethionic acid	$EA_2.2HO$
Sulphate of carbyl....	$EA_2.2A$
Glycolic acid	$OtO_2.2HO$
Sulphacetic acid.....	$OtA_2.2HO$
Diethylenic glycol	$\left(\begin{smallmatrix}C_4H_4O_2\\C_4H_4O_2\end{smallmatrix}\right).2HO$
Ethionic acid	$\left(\begin{smallmatrix}C_4H_4O_2\\S_2O_4O_2\end{smallmatrix}\right).2HO$
Disulphoetholic acid ..	$\left(\begin{smallmatrix}C_4H_4(S_2''O_4)\\S_2O_4O_2\end{smallmatrix}\right).2HO$
Sulphoglycolic acid ..	$\left(\begin{smallmatrix}C_4H_4O_2\\S_2O_4O_2\end{smallmatrix}\right).2HO$

In all these cases we have either sulphuric or sulphurous anhydride functioning as oxygen in glycol, or acting as oxide of ethylene in the polyethylenic glycols. Perhaps this will be more obvious if we compare isethionic anhydride, although its separate existence is still doubtful, with oxide of ethylene and with sulpho-naphthalin, the separate existence of which is established:—

Oxide of ethylene.....	$C_4H_4.O_2$
Isethionic anhydride.....	$C_4H_4.S_2O_6$
Sulpho-naphthalin	$C_{20}H_8.S_2O_6$

But even if we had no such clear instances of anhydrides taking the place of the oxygen attached to the secondary radicle, we have so many examples of this complete atomic substitution in organo-metallic bodies that we could not hesitate in admitting the possibility of such replacements. It will suffice to quote the following cases in regard to the oxide of zinc:—

Oxide of zinc	$Zn_2 \begin{cases} O \\ O \end{cases}$
Zinc-methyl	$Zn_2 \begin{cases} C_2H_3 \\ C_2H_3 \end{cases}$
Dinitromethylate of zinc	$\begin{matrix} Zn \\ C_2H_3 \end{matrix} \begin{cases} NO_2 \\ NO_2 \end{cases}$
Methyldithionate of zinc	$\begin{matrix} Zn \\ C_2H_3 \end{matrix} \begin{cases} SO_2 \\ SO_2 \end{cases}$

Guthrie's compounds of amylene and ethylene with peroxide of nitrogen ($C_{10}H_{10}.2NO_4$ and $C_4H_4.2NO_4$) (Qu. J. Chem. Soc., xiii., 129) will naturally occur as illustrations. By admitting that anhydrides may function as oxygen in oxides, we are relieved from the difficulties attending the explanation of the constitution of salts which have an excess of an anhydride, as in the case of the chromates of potash, which now are seen to represent the oxides of potassium:—

Binoxide of potassium....	$K_2O_2.O_2$	Chromate of potash....	$K_2O_2.Cr_2''O_6$
Teroxide.....(?)	$K_2O_2.O_4$	Bichromate of potash ..	$K_2O_2.2Cr_2''O_6$
Tetroxide	$K_2O_2.O_6$	Terchromate of potash..	$K_2O_2.3Cr_2''O_6$

Having now explained the general views upon which I contend that anhydrides function oxygen in the completion of a deficient atomicity of an oxide, it is necessary to examine whether these views are sufficient to explain the various classes of salts. Neglecting for the present the mixed oxides and suboxides, the following are the main classes of oxides which present themselves; in formulating them, the symbol R represents such elements as nitrogen, phosphorus and arsenic, and M such metals as manganese or iron.

	Atoms.		Molecules.
1. Protoxides	MO	or	M_2O_2
2. Teroxides and sesquioxides	RO_3 or M_2O_3	or	R_2O_6 or M_4O_6

3. Peroxides	MO_2	or	$\begin{cases} RO_4 \\ \text{or} \\ M_2O_4 \end{cases}$
4. Nitric acid type.....	RO_5	or	R_2O_{10}
5. Manganic	MO_3	or	M_2O_6

In addition to these, and beyond the manganic acid type, we have the permanganic acid Mn_2O_7, and a still higher oxide in the case of potassium, where, however, the basylous character of the element is not yet converted into a chlorous function by the eight atoms of oxygen in the tetroxide KO_4 or K_2O_8.

It will be seen, as I proceed, that although all these oxides must be borne in mind, in order to understand the struggle for a completed atomicity, yet that a limited number of them is quite sufficient to use as types for classification. We may at once neglect the detailed consideration of the *atomic** protoxide MO, because it ranges itself in Gerhardt's class of HH or HCl, which, large and comprehensive as it is, enforces our complete acquiescence. We pass then to the next oxide of the series, the teroxide in the cases of such elements as nitrogen and bismuth, and the sesquioxide of the metals generally.

Teroxide Type.

The teroxide type has been fully studied in the beautiful investigations of Hofmann, so far as regards one important class of its derivatives on the general atomic type of the class ammonia NH_3. It will be unnecessary for me, especially as this has already formed the subject of one of your lectures, to dwell upon this important member of the class, and I therefore pass to the consideration of the other bodies which I propose to group under this atomic type, which, as in the previous cases described, has the atomic form RO_3 and the molecular form $R_2O_6 = R_2O_3.O_3$. The teroxide type receives its fittest illustrations in nitrous, phosphorous, arsenious, antimonious, bismuthous, and boracic anhydrides. The probable *atomic* constitution of these teroxides is $RO_2.O$. For this expression there is abundance of evidence even

* I would here mention, once for all, that although I frequently formulate the *atom* of a body in order to show its active chemical character and inner constitution, that I accept as a general rule four-volume formulæ for molecules, the completed symmetry of which however would not explain the chemical activity of the body.

when, as in the case of arsenic, we have no clear proof of the separate existence of the radicle RO_2. But we have cacodyl $As(C_2H_3)_2$, its oxide $As\left\{\begin{matrix}(C_2H_3)_2\\O\end{matrix}\right.$, and corresponding sulphide and chloride; and we have this atomic structure receiving direct confirmation in arsenious dioxmethide $AsO_2.C_2H_3$, and its sulphur analogue $AsS_2.C_2H_3$. Again, looking at Frankland's researches (Chem. Soc. J. xv, 363) on the boron compounds, we find the radicle BO_2 forming a methide and ethide, the latter of which acts as an acid, and unites with water and ether as follows:—

Dihydrate of boric dioxethide $BO_2.C_4H_5.2HO$
Diethylate „ „ $BO_2.C_4H_5.2(C_4H_5O)$.

To support the radicle in oxide of bismuth, we have Schroeder's discovery of the binoxide BiO_2, and we find its analogue in dichlorethide $BiCl_2.C_4H_5$. In regard to antimony we are familiar with Peligot's chloride and iodide of antimonyl $SbO_2.Cl$ and $SbO_2.I$.

As respects phosphorus, every theory admits the existence of phosphoryl PO_2. We are, therefore perfectly justified by our knowledge in writing the *atoms* of teroxides $RO_2.O$, although, for convenience of comparison, I prefer to write it arbitrarily as $R\left\{\begin{matrix}O_2\\O\end{matrix}\right.$. The analogies of sesquioxides to the teroxides are so obvious that few would be inclined to separate them; and yet their formula M_2O_3 is distinct from that of the teroxide RO_3. Some of the sesquioxides, like those of nickel and cobalt, act to acids exactly as if they were constituted of peroxides united to protoxides $MO_2.MO$, and sesquioxide of manganese comports itself thus in a less decided manner; but many other oxides of this class, such as those of uranium, chromium, iron, and aluminum, behave as if they contained protoxides as radicles $M_2O_2.O$. On the first view, the relation of teroxides to sesquioxides is obvious—an atom of a protoxide taking the place of an atom of oxygen:—

Teroxides..... $R\left\{\begin{matrix}O_2\\O\end{matrix}\right.$
Sesquioxides ..... $M\left\{\begin{matrix}O_2\\MO.\end{matrix}\right.$

However, as our knowledge does not justify this general assump-

tion, and as it is probable that there are varieties in the constitution of the numerous members of this group, we prefer to write the *atoms* of these oxides in the arbitrary formula $M_2 \begin{cases} O_2 \\ O. \end{cases}$

It is a notable characteristic of basic sesquioxides, that they unite with one or with three atoms of acid, just as the acid teroxides affect one or three atoms of base. The biatomic type is rarer and not so well defined. To compare this properly, we select three salts from Bloxam's* paper on the arsenites, and compare them with known salts of peroxides of iron :—

Arsenite of zinc	$AsO_3.3ZnO$	Persulphate of iron	$Fe_2O_3.3SO_2O$
,, magnesium	$AsO_3.2MgO$	Binacetate of iron†	$Fe_2O_3.2C_4H_3O_2.O$
,, ammonium	$AsO_3.NH_4O$	Mononitrate of ferric oxide‡	$Fe_2O_3.NO_4O.$

It is clear from such a comparison that these compounds are atomically similar, this variety being mainly due to the fact that, in one case, the atomicity is gratified by chloroids, in the other case by basyls. In fact, we not unfrequently find sesquioxides affecting either of these according to circumstances, as sesquioxide of uranium in uranate of soda $U_2O_3.NaO$, and as nitrate of uranium $U_2O_3.NO_4O$. Vanadic acid, in like manner, though usually taking up basyls, forms a well marked sulphate $VO_3.3SO_3$. Alumina, chiefly affecting chloroids, still shows us in *Spinelle-ruby* ($Al_2O_3.MgO$), and in *Gahnite* ($Al_2O_3.ZnO$), that it can unite with basyls. Then, again, for every compound of an acid with a sesquioxide we have a corresponding hydrate, in which water represents the chloroids. We may, therefore, safely assert that the mere difference as to whether an oxide gratifies its wanting atomicity by chloroids or by basyls, forms no ground for separating them into distinct types. But if we are led to this conclusion, with regard to teroxides and sesquioxides, from observing their common disposition to unite with one or with three atoms, either of basyls or chloroids, it becomes both natural and logical to examine whether all tribasic anhydrides should not be brought into the same type. When we review Frankland and Buckton's researches on organo-metallic bodies, we find abundant illustrations that the radicle phosphoryl (PO_2) and arsenyl (AsO_2) play a yet

* Chem. Soc. Jour., xv, 298.

† Crum, Chem. Soc. Journ.

‡ See also Parkman, American Jour. of Science, xxxiv, p. 321, for monocarbonates of sesquioxides and teroxides.

more intimate part in the pentacids by assuming in fact the function of the primary radicles P and As in the teroxides:—

Phosphorous anhydride.....	P	$\left\{\begin{matrix}O_2\\O\end{matrix}\right.$
Phosphoric „	PO_2	$\left\{\begin{matrix}O_2\\O\end{matrix}\right.$

A very few remarks will indicate the grounds on which we demand this new function for phosphoryl in phosphoric acid. For this purpose, the following illustrations will suffice:—

Arsenic-dioxidichlormethide	AsO_2	$\left\{\begin{matrix}Cl_2\\C_2H_3\end{matrix}\right.$
Cacodylic anhydride	AsO_2	$\left\{\begin{matrix}(C_2H_3)_2\\O\end{matrix}\right.$
Sulphocacodylic anhydride	AsS_2	$\left\{\begin{matrix}(C_2H_3)_2\\S\end{matrix}\right.$
Dioxide of Phosphethylia	PO_2	$\left\{(C_4H_5)_3\right.$
Disulphide „	PS_2	$\left\{(C_4H_5)_3\right.$

In all these cases we find binoxides or bisulphides acting apparently as primary radicles. We have now only to compare the teroxides, sesquioxides, and tribasic acids to see that they have a similar constitution with varying primary radicles:—

Teroxides	R	$\left\{\begin{matrix}O_2\\O\end{matrix}\right.$
Sesquioxides.....	M_2	$\left\{\begin{matrix}O_2\\O\end{matrix}\right.$
Pentoxides*	RO_2	$\left\{\begin{matrix}O_2\\O.\end{matrix}\right.$

Before discussing the reasons of these mono- or triatomicities, it will be well to allude to the ether of glycerin and to glyceric anhydride, which are obviously constructed on the type of the sesquioxides:—

Ether of glycerin	(C_6H_5)	$\left\{\begin{matrix}O_2\\O\end{matrix}\right.$
Glyceric anhydride	$(C_6H_3O_2)$	$\left\{\begin{matrix}O_2\\O\end{matrix}\right.$

* Nitric acid, generally acting as a monobasic acid, is probably $NO_4.O$ instead of $(NO_2)O_2.O$. We see the change of radicle in this class of salts when nitric acid acts on arsenious acid $AsO_2.O + NO_4.O = NO_2O + AsO_4.O$.

It would be a waste of time to support this analogy by the extensive series of chlorhydrins described by Berthelot and Luca.* In like manner as glyceric acid is built up by the oxidation of the olefines (Allylene) C_6H_4, so citric acid, a well defined tribasic acid, may be supposed to have its primary radicle derived from hexylene $C_{12}H_{12}$, or the secondary radicle, hexyl $C_{12}H_{13}$.

Citric anhydride ..... $(C_{12}H_5O_8)\left\{\begin{matrix}O_2\\O\end{matrix}\right.$

In all the previous formulæ, we have divided the oxygen external to the radicle, with the view of explaining more readily their varying atomicities. The next oxide to the teroxide in the series of oxides is the peroxide type, a position of repose and neutrality, and which from this circumstance is typical of many salts. A teroxide only requires one atom to reach this stage, which is represented by NO_4 in the nitrogen class, and by Mn_2O_4 in the metallic oxides. A single atom of a basyl or of a chloroid will suffice for the peroxides, or the sesquioxides, to reach this period of repose. Let us, representing chloroids by A, and basyls by B, indicate this completion of an unsymmetrical atom.

Peroxide of	nitrogen	NO_3O	mono-arsenite $AsO_3.B$
,,	metal	$M_2O_3.O$	mono-sesquisalt $M_2O_3.A$.

But in a peroxide, although a stage of repose is attained, there is yet incomplete gratification of atomic affinities, and passing over for the moment the nitric acid type, the next stage is represented by manganic anhydride, $Mn_2O_6=Mn_2O_4.O_2$., or $Mn_2O_3.O_3$. If we tabulate a few examples of this type, the triatomic power of the oxides under consideration will be very apparent. For simplicity we formulate sesquisalts and their analogues as corresponding to the double teroxide $R_2O_3.O_3$—thus $R_2O_3.A_3$—but it is obvious that they may be put intelligibly on the manganic acid type, $Mn_2O_4.O_2$ —thus $M_2O_3A.A_2$. Example: $Fe_2O_3,NO_4.O,2(C_4H_3O_2)O$—one of the nitro-acetates of iron.

Molecule of	teroxides	$R_2O_3.O_3$	..	sesquisalts	$M_2O_3.A_3$
,,	manganic anhydride	$M_2O_4.O_2$	..	,,	$(M_2O_3A).A_2$

* Ann. Ch. Phys. [3] lii, 433.

Molecule of Sesquioxides $M_4O_3.O_3$	..	Molecule of Penta-anhydrides	$(RO_2)_2O_3.O_3$
Glycerin..... $(C_6H_5)O_3.3HO$	..	Glycerides	$(C_6H_5)O_3.A_3$
Phosphoric acid .. $(PO_2)O_3.3HO$	..	Phosphates	$(PO_2)O_3.B_3$
Ferricyanide of potassium — $Fe_2Cy_3.3KCy$	..	Double chloride of iron and potassium	$Fe_2Cl_3.3KCl$

From the remarks which have preceded, it is obvious that both the monobasic and tribasic character of teroxides and pent-oxides are necessary for the establishment of a period of stability in one case and of saturation in the other. But the assumption of a bibasic character is not so easy of explanation, either on this view or on the water-type, unless indeed we assume that such bodies as the pyrophosphates are compounds formed by the union of ortho-, with metaphosphates (Odling's Chemistry, p. 300). Of course the difficulty ceases altogether if we place them on the nitric acid or pentacid type: for then $NO_3.2O$ is analogous to $RO_3.2A$, or $RO_3.2B$. It ceases also if we believe, what may be possible when we recollect the results of their electrolysis, that there are different radicles in the three kinds of phosphates, similar to the changes which take place in propyl when its hydrogen is subtracted, thus:—

Metaphosphates	$PO_4\ \{O\ B$	like salts of Propylic ether	$C_6H_7\ \{O\ A$
Pyrophosphates	$PO_3\ \{O_2\ B_2$	like salts of Propylene ether	$C_6H_6\ \{O_2\ A_2$
Orthophosphates	$PO_2\ \{O_3\ B_3$	Glycerides	$C_6H_5\ \{O_3\ A_3$

I do not therefore profess to solve this difficulty, which is as great on the water-type, if we attempt to preserve simplicity; for pyrophosphoric acid cannot be written as constructed on 4 atoms of water $\left.\begin{matrix}PO_3''\\H_2\end{matrix}\right\}O_4$ without breaking the unitary system, and must be made as 8 atoms of water, $\left.\begin{matrix}P_2O_6''''\\H_4\end{matrix}\right\}O_8$.

Before leaving this part of the subject, I would remark, in conclusion, that we do not find perfect neutrality in the salts of the teroxide type, as we generally do on those of the peroxide: for when the basyls complete the wanting atomicities, an alkaline

character is generally impressed on the product, or the reverse, when chloroids are employed in the completion. But this result is what we would expect in the case of bodies built up on such a high condition of completed atomicity as manganic acid. I would also in this place refer to a circumstance which might naturally be brought as an objection to my views, viz., that in some cases the base is used as the body whose wanting atomicity is to be completed, while in other cases reference is made to the acid. But in all instances of combination, there is both action and reaction between the two classes of bodies. The very chemical activity of the basyl on the one hand, and of the chloroid on the other, shows that both of them have their atomicities incomplete, and that both require atomic saturation. It is therefore necessary to look at the atomic wants both of the basyls and of the chloroids entering into combination. It depends in fact upon the atomicities which are to be gratified whether the base determines the character of the compound, or whether the acid plays the predominant part in producing the result, or whether they neutralise each other.

Peroxide Type.

This type embraces a large class of compounds, which can only be brought under your notice by a few general examples. It is obvious that there may be three different forms under which salts on the peroxide type may occur.

1.....	MO.O	in salts	MO.A. or MO.B
2.....	$M_2O_2.O_2$	,,	$M_2O_2.A_2$ or $M_2O_3.B_2$
3.....	$M_2O_3.O$	,,	$M_2O_3A.$ or $M_2O_3.B$

All three varieties are included under the two modifications of the type MO_2 or M_2O_4. The first of these may be illustrated by binoxide of sodium NaO_2, or peroxide of hydrogen HO_2; the second by the peroxide of tin Sn_2O_4. It will be convenient to consider each modification separately.

1. *Type—Peroxides of Uniatomic Metals* MO.O.

The molecules of protoxides and sulphides of the metals range themselves under this type. Thus, following the type of binoxide of sodium NaO.O, we have the molecule of soda NaO.NaO, its hydrate NaO.HO., and any neutral salt of soda, NaO.A. All

derivatives of these also are included, as NaS.NaS ; NaS.HS. ; NaS.A. As the basylous protoxides and their derivatives range themselves under this type, so also do the chlorous molecules of a like order, for example, hypochlorous anhydride ClO.ClO, the protochloride of sulphur ClS.ClS., hypochlorous acid ClO.HO, and a hypochlorite ClO.NaO. The radicles which in the molecules of their protoxides come under this division of the class, may be compound as well as simple, as in basylous oxide of ammonium $NH_4O.NH_4O$ or chlorous nitric anhydride $NO_4O.NO_4O$, or in their better known hydrates $NH_4O.HO$. and $NO_4O.HO$. The anhydrides and acids of the nitric acid class, and the oxides and hydrates of the monamines, naturally include themselves in this class, as in the case of arsenic anhydride $AsO_4O.AsO_4O$, arsenic acid $AsO_4O.HO$, and hydrated oxide of tetrethylarsonium $As(C_4H_5)_4O.HO$.

The oxides, chlorides, sulphides, &c., of biatomic radicles find themselves arranged in this division. Just as tin gives us Sn_2O_2, Sn_2S_2, Sn_2Cl_2, so we have corresponding compounds of ethylene EtO_2, EtS_2, $EtCl_2$; and on the chlorous side we have such compounds as carbonic anhydride $C_2O_2.O_2$, sulphuric anhydride $S_2O_4.O_2$, succinic anhydride and chloride $C_8H_4O_4.O_2$, and $C_8H_4O_4.Cl_2$. As the hydrates and salts of monotomic bases and acids are included in this division, it embraces the large class of alcohols and ethers, of which methylic alcohol is the starting point: thus we have ethyl ether $C_4H_5O.C_4H_5O$, like methyl-ethyl ether $C_4H_5O.C_2H_3O$, or like alcohol $C_4H_5O.HO$, or acetic ether $C_4H_5O.C_4H_3O_2.O$. So with the oxidised derivatives we have acetic anhydride $(C_4H_3O_2)O.(C_4H_3O_2)O$, acetic acid $(C_4H_3O_2)O.HO$, and acetate of sodium $(C_4H_3O_2)O.NaO$.

It may be objected to this view that we arrange under this division a large number of bodies with the typical peroxides of which we are not acquainted. But after the beautiful discovery by Brodie* of the peroxides of acetyl and succinyl, no one will be inclined to deny their possible existence, while the mere fact of so many of them, either as acids or as bases, showing incomplete saturation, renders to my mind their future discovery probable.

The second division of this class, viz., $M_2O_4 = M_2O_2.O_2$ is more extensive than the first. In the first place we find the biatomic alcohols and bibasic acids generally. The following examples will show their relation to the type $M_2O_2.O_2$:—

* Proc. Royal Soc., ix, 361.

Ethylene glycol. . . .	$(C_4H_4)O_2.2HO$	Glycollic acid	$(C_4H_2O_2)_2.O.2HO$
Ethylenate of sodium	$(C_4H_4)O_2.2NaO$	Glycollate of soda	$(C_4H_2O_2)O_2.2NaO$
Acetate of ethylene	$(C_4H_4)O_2.2\bar{A}$	Sulphacetic acid	$(C_4H_2O_2)(SO_3)_2.2HO$
Monacetate „	$(C_4H_4)O_2 \left\{ \begin{matrix} HO \\ \bar{A} \end{matrix} \right\}$	Binoxalate of potash.	$(C_4O_4)O_2.\left\{ \begin{matrix} KO \\ HO \end{matrix} \right.$
Ethylene-mercaptide of ethyl	$(C_4H_4)S_2 \left\{ \begin{matrix} C_4H_5S \\ HS \end{matrix} \right.$	Tartrovinic acid	$(C_8H_4O_8)O_2.\left\{ \begin{matrix} C_4H_5O \\ HO \end{matrix} \right.$
Aceto-butyric glycol	$(C_4H_4)O_2 \left\{ \begin{matrix} (C_4H_3O_2)O \\ (C_8H_7O_2)O \end{matrix} \right.$	Tartrate of antimonyl and potassium	$(C_8H_4O_8)O_2.\left\{ \begin{matrix} SbO_2.O \\ KO \end{matrix} \right.$

Wurtz has already pointed out in his lecture to the society (Chem. Soc. Journ., xv. 387), as Kekulé has also done (*Lehrbuch*, i. 1058), that the diethylenic alcohols find their analogues not only in oxides which coalesce and unite with water, but also more completely in the case of sulphuric acid and the Nordhausen acid. The following Table will put this in a still more comprehensive view, if we represent the respective glycol-ethers by symbols to save repetition:—

Oxide of ethylene $C_4H_4O_2$ = Eg
Oxide of sulphuryl $S_2O_4O_2$ = Sg
Oxide of chromyl $Cr_2O_4O_2$ = Crg

Glycol	$Eg . 2HO$	. . . . Sulphuric acid	$Sg . 2HO$
„ (diethelenic)	$Eg_2 . 2HO$	. . . . Nordhausen „	$Sg_2 . 2HO$
K. „ „	$Eg_2 . 2KO$	. . . . . Bichromate of potash . .	$Crg_2 . 2KO$
Glycol (triethelenic)	$Eg_3 . 2HO$	. . . . Terchromate „ . .	$Crg_3 . 2KO$
Glycol-chlorhydrin	$Eg . HCl$	. . . . Sulphuric chlorhydrin . .	$Sg . HCl$
Monoxethelamine	$Eg . HNH_2$	. . Sulphamic acid	$Sg . HNH_2$
Dioxethelamine	$Eg_2 . HNH_2$	. . . . Chlor-sulphate of sodium	$Sg . NaCl$
Dichlorhydrin	$Eg_2 . HCl$	. . . . . Peligot's salt.	$Crg . KCl$

The above examples must suffice to show that biatomic alcohols and their derivatives, and bibasic acids, may readily be included in this division. In it are also embraced peroxides, sulphides, and chlorides, as carbonic and silicic anhydrides, C_2O_4 and Si_2O_4, bisulphide of carbon C_2S_4, and tetrachloride of silicon Si_2Cl_4, and similar compounds of tin, manganese, strontium, &c.

It may be less obvious how suboxides may be placed in this division; but as we have already shown that the atomicity of a body may be indifferently gratified, either by chlorous or by basylous atoms, in the general type $M_2O_2.R_2$. the terms R_2 may either be filled up by oxygen, as in a peroxide, or by a basyl. This we see in peroxide of tin $Sn_2O_2.O_2$, and stannic oxydiethide $Sn_2O_2(C_4H_5)_2$ where 2 atoms of ethyl take the place of 2 atoms of oxygen in

the peroxide. In like manner, suboxide of lead $Pb_2O_2.Pb_2$ represents peroxide of lead in which 2 atoms of oxygen are replaced by 2 atoms of lead; and suboxide and subchloride of copper $Cu_2O_2.Cu_2$ and $Cu_2Cl_2.Cu_2$ have a like atomic constitution, in this respect exactly resembling the chloride of stannic diethide, $Sn_2Cl_2(C_4H_5)_2$, and the sulphide of stannic dimethide $Sn_2S_2\ (C_2H_3)_2$.

Lastly we come to the third division of this class, viz., when a sesquioxide completes its atomicity as a peroxide by assuming a single atom of a chloroid or of a basyl, the form of the type now being $M_2O_3.R$. All the magnetic oxides and sulphides range themselves under this division, the term R being filled up by a protoxide, a protosulphide, water, or a single atom of an anhydride.

Typical oxide	$M_2O_3.R.$
Magnetic oxide of iron	$Fe_2O_3.FeO$
Hydrate of sesquioxide of iron ..	$Fe_2O_3.HO$
Chrome iron ore	$Cr_2O_3.FeO$
Red oxide of manganese	$Mn_2O_3.MnO$
Hydrate of sesquioxide of manganese..	$Mn_2O_3.HO$
Aluminate of soda	$Al_2O_3.NaO$
„ zinc	$Al_2O_3.ZnO$
Protocarbonate of alumina	$Al_2O_3.CO_2$
Acetate of uranium	$U_2O_3.C_4H_3O_3$
Silicate of iron	$Fe_2O_3.SiO_2$
Chlortriplumbethide	$Pb_2(C_4H_5)_3.Cl$
Oxisesquistannic trimethide	$Sn_2(C_2H_3)_3.O$

These examples, showing that the wanting atom may be filled up either by chlorous or by basylous bodies, will suffice to explain how it is that magnetic oxides and anomalous salts of sesquioxides naturally range themselves under this division.

Having incidentally said so much regarding the manganic acid and nitric acid types, we will pass them over for the present, as it is necessary to curtail the lecture within proper dimensions, and refer you, in conclusion, to the tetroxide type.

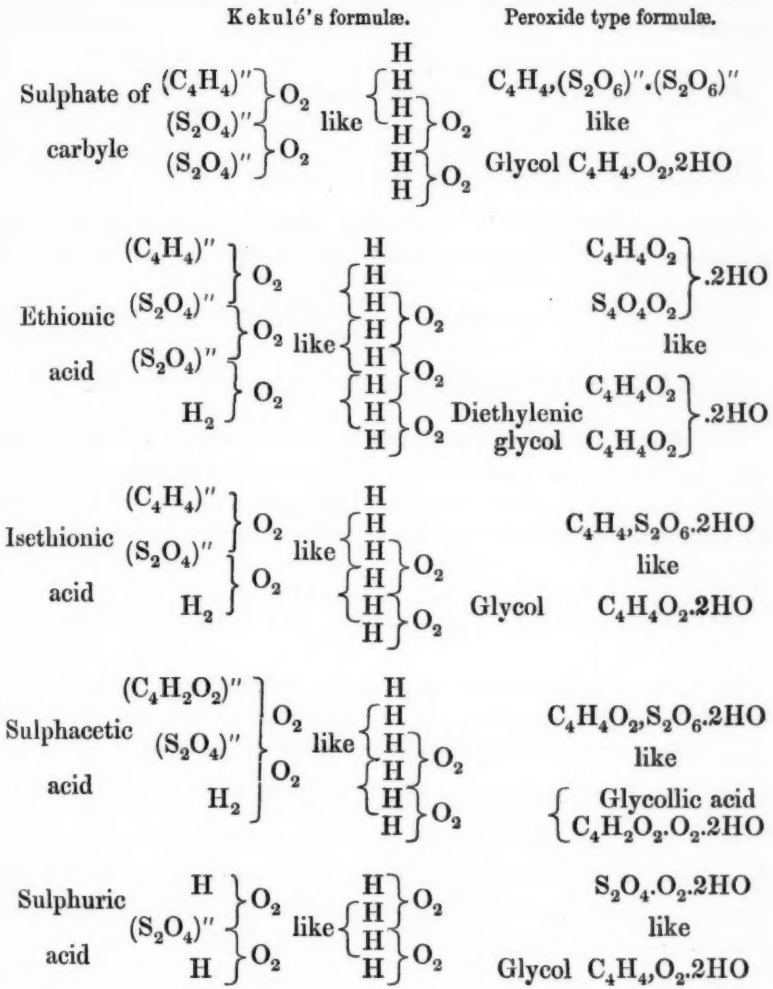
Tetroxide Type.

This type, expressed by the formula MO_4 or M_2O_8, has a very limited range, and might possibly disappear altogether if we were

better acquainted with it. Nevertheless there are a few compounds which, at present, require this type for their explanation.

The first example which occurs is that of the tetroxide of potassium KO_4 or K_2O_8, which we have also represented in the sulphides of potassium K_2S_8, and of sodium Na_2S_8. We find it also in the hydrates of the binoxides as $Sn_2O_4.4HO$, stannate of soda $S_2O_4.4NaO$, and in the salts $M_2O_4.4A$. It also occurs rarely in certain salts in which anhydrides enter into combination with the base in multiple proportions, as in terchromate of potash $K_2O_2.3Cr_2O_6$. This type, however, is indirectly necessary, as showing the highest state of atomic saturation with which we are acquainted in the metallic oxides, and to which many of them tend in completing their atomicities. Thus the complete saturation of M_2O_8 is shown in a permanganate M_2O_7B, in which the last atom of oxygen is filled up by a basylous body. The attainment of this highest atomic saturation for oxides is also observed in the salts of acids of the manganic acid type, as S_2O_62B, or of the tribasic nitric acid type $NO_5.3B$, in which the general point of atomic saturation RO_8 or M_2O_8 is obtained. But, although the tetroxide is the highest point of atomic saturation in the case of the metals, the compound radicles which play their part in the chlorous metallic compounds throw them into types of greater simplicity than this one.

In the preceding portion of the lecture I have endeavoured to show how chemical compounds may be classed under four types, viz., the type of hydrochloric acid, that of a peroxide, teroxide, and tetroxide. In Gerhardt's classification, the type of water is made to alter in magnitude from $H_2O_2...H_4O_4$ to H_nO_n; while in those upon which my classification is based, the only two divisions of a type (except in the case of polyethylenic alcohols, the oxides and the compounds which they represent) are two in number, as represented in the peroxide MO_2 or M_2O_4. With this small limit to classification, there is no difficulty in arranging under the four types, all substances which I have tried to include under them. But it still remains for me to show by contrast whether the types of Gerhardt or those which I advocate give the simplest expression in cases of difficulty. I select for this purpose the compounds of sulphuric anhydride with the olefines to bring the two systems into comparison. I take a few of these, as formulated by Kekulé, and place beside them the formulæ on the type of peroxides.



It will be observed that the formulæ on the peroxide type, besides being much simpler in expression, keep to the type glycol (or the peroxide type) throughout, while the formulæ as given by Kekulé alter in value according to the difficulties of the explanation. I now bring into comparison some of the equations of decomposition which are thought particularly to support the water type, in order to show that they receive at least an equally simple expression on the oxide types. Let us take, for instance, the

formation of acetate of ethylene as represented on the two types:—

$$(1)\ C_4H_4I_2 + 2\left(\left.\begin{matrix}C_4H_3O_2\\Ag\end{matrix}\right\}O_2\right) = 2AgI + \left.\begin{matrix}(C_4H_4)''\\C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_4$$

$$(2)\ C_4H_4I_2 + 2(AgO.C_4H_3O_3) = C_4H_4O_2.2C_4H_3O_3 + 2AgI$$

If we now take Geil's* method of preparing acetic or benzoic anhydride, the equations on the two systems are the following:—

$$(3)\ 2\left\{\begin{matrix}C_4H_3O_2\\Cl\end{matrix}\right\} + Ba_2O_2 = \left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2 + 2BaCl.$$

$$(4)\ 2(C_4H_3O_2.Cl) + 2BaO = 2(C_4H_3O_2.O) + 2BaCl.$$

The simplicity of the peroxide type becomes however more apparent when the equations of decomposition involve a change in the atomicity. Thus, when sesquioxide of nickel is acted on by hydrochloric acid, the equation on the water type is the following:—

$$(5)\ \left.(Ni^{\frac{2}{3}})_4\right\}O_6 + 6\left.\begin{matrix}H\\Cl\end{matrix}\right\} = 4\left.\begin{matrix}Ni'\\Cl\end{matrix}\right\} + 3\left.\begin{matrix}H\\H\end{matrix}\right\}O_2 + Cl_2.$$

In this equation nickel on one side represents only $\frac{2}{3}$ of the atomicity which it affects on the other side. On the peroxide type the equation, without change of atomicities, is—

$$(6)\ Ni_2O_2.O + 3HCl = Ni_2Cl_2 + 3HO.$$

The difference will be still more apparent if we represent the formation of peroxide of hydrogen by Duprey's method of passing carbonic acid through peroxide of barium suspended in water:—

$$(7)\ \left.\begin{matrix}Ba''\\Ba''\end{matrix}\right\}O_4 + \left.\begin{matrix}H'\\H'\end{matrix}\right\}O_2 + C_2O_2''\Big\}O_2 = \left.\begin{matrix}Ba'_2\\C_2O_2\end{matrix}\right\}O_4 + 2H''\Big\}O_2$$

In this equation we have not only barium with a biatomic power on one side and a monoatomic power on the other, but we have hydrogen itself equal to one atom of itself on one side and equal to two atoms of itself on the other side of the same equation. On the peroxide type, the formation of peroxide of hydrogen is

* Geil, Comptes rendus, lvi, 360.

represented as follows, without any change in the atomicities of the radicles:—

8. $Ba_2O_2.O_2 + H_2O_2 + C_2O_4 = H_2O_2.O_2 + Ba_2O_2.C_2O_4$.

I have in this lecture endeavoured to compress within reasonable limit the views which I entertain in regard to the constitution of salts. The main support of these views consists in the gratification of certain atomic affinities possessed by the combining radicles, the atomicity being capable of saturation either by basylous or chlorous radicles,—themselves generally bodies possessing the character of radicles by being in a state of unsatisfied atomic union. I fear that these views are too far apart from those which are yet doing such good service to chemistry to receive general acceptance; but I fancy that I do not do a disservice to our science when I invite you to look upon chemical compounds under various aspects.

XXXV.—*Note on a Compound of Dextro-glucose with Bromide of Sodium.*

By John Stenhouse, L.L.D., F.R.S.

Two equivalents of glucose (prepared from starch by means of sulphuric acid) and one equivalent of bromide of sodium were dissolved in a small quantity of water, and the solution set aside in a warm place to evaporate spontaneously.

The crystals which were deposited, after having been slightly washed with cold water, were twice crystallised from boiling alcohol.

For the description of their crystalline form and determination of their angles, which are appended at the close of this notice, I am indebted to my friend, Professor W. H. Miller, of Cambridge.

The compound was subjected to analysis in the usual way:—

I. ·4435 gramme, dried at 100° and burnt with chromate of lead, gave ·5045 gramme carbonic acid and ·207 gramme water.

II. ·374 gramme gave ·428 gramme carbonic and ·169 gramme water.

III. 1·267 gramme dried at 100° gave ·513 gramme bromide of silver.

		Theory.	I.	II.	III.
C_{24}	= 144 =	31·11	31·02	31·21	—
H_{24}	= 24 =	5·18	5·18	5·02	—
O_{24}	= 192 =	41·47	—	—	—
Na	= 23 =	4·96	—	—	—
Br	= 80 =	17·28	—	—	17·23
	463	100·00			

From these analyses it follows therefore that the formula of the compound is $C_{24}H_{24}O_{24}$,NaBr.

This compound is evidently anhydrous, as, after drying in vacuo, it did not lose weight by prolonged exposure to 100°C. The corresponding compound with chloride of sodium was discovered by Calloud, and has been analysed by Lehmann, Erdmann, Soubeiran, and others.

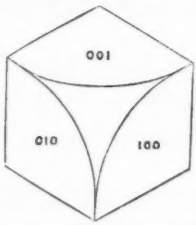
Professor Miller's Determinations of the Compound of Glucose and Bromide of Sodium.

Rhombohedral	..	111	100 = 64° 56′
Observed form	..	—	100

Normals to any two of the faces 100, 010, 001 make with one another an angle of 103°20′. The solid angle formed by the faces 100, 010, 001, is rounded off as if by imperfectly formed faces of the form 111, and those of an obtuse rhombohedron in inverse position. The faces of the form 100 are uneven, and consequently the angles given above, though deduced from the measurement of sixty-four dihedral angles must be regarded as rough approximations. Some of the crystals were obtained from a solution in water, others from a solution in alcohol. The latter were rather better than the former.

No cleavage observable. The spheroidal wave-surface is prolate. When a crystal, immersed in oil contained in a vessel having parallel sides of glass, is placed in a polarizing apparatus, the rings of a uniaxial crystal can be seen through opposite faces of the form 100. In parts of the crystal the rings are sometimes distorted, probably by a strain, so as to exhibit the appearance of two axes making a small angle with one another.

These crystals appear to be isomorphous with those of the compound of glucose with chloride of sodium, described by Von Kobell (*J. pr. Chem.*, xxviii., 489), and under a different name by Schabus (*Bestimmung der Krystallgestalten*, 21). See Rammelsberg (*Handbuch der Krystallographischen Chemie*, 399; and *Die Neuesten Forschungen in der Krystallographischen Chemie*, 217).



The decidedly rhombohedral character of the compound of glucose and bromide of sodium, and the approximation of its angles to those of the compound of glucose and chloride of sodium is unfavourable to Pasteur's view of the form of the latter (*Ann. Ch. Phys.*, [3] xxxi., 92), and renders it probable that the very curious appearance when examined by polarized light, observed by Des Cloizeaux (*Annales des Mines*, xi. 324; xiv. 33.), must be due to a state of strain.

Cane-sugar and chloride of potassium when dissolved in atomic proportions and left to spontaneous evaporation, deposited crystals containing both cane-sugar and chloride of potassium. Analysis, however, proved them to be merely mixtures, and not definite compounds, the amount of chlorine being found to vary considerably, and in every instance to be much below the calculated quantity.

XXXVI.—*Note on Nitro-erythroglucin.* $C_8H_6(NO_4)^4O_8$.

By John Stenhouse, L.L.D., F.R.S.

In the analysis of this compound, which I published in the Phil. Trans. for 1849 (page 399), the carbon was found to be more than half per cent. too high, and the nitrogen a little too low. I have recently prepared a new quantity of the substance, and re-examined it with the following results. Pulverised erythroglucin added by small portions to fuming nitric acid, which is to be kept cool, dissolves, with considerable rise of temperature, and if the solution be mixed with a quantity of oil of vitriol equal in weight to the nitric acid, or rather more, the whole forms, in half-an-hour, a

crystalline magma, which is collected on a funnel plugged with asbestos, washed with cold water, pressed between paper, and recrystallised from hot alcohol.

Eight grammes of erythroglucin and two ounces of fuming nitric acid gave 14·5 grammes of purified nitro-compound.

I. ·3965 gramme substance ignited with oxide of copper gave ·2330 gramme of carbonic acid and ·075 water.

II. ·5150 gramme gave ·3000 gramme of carbonic acid and ·0986 gramme water.

III. ·2725 gramme substance gave, by Dumas' method, 43·5 c.c. of nitrogen at 10°C. Bar. corrected to 0° = 742·4 millim. Tension of water-vapour at 10° = 9·1 mil. Corrected pressure = 733·3 m.m.

43·5 c.c. nitrogen at 10°C. and 733·3 m.m. = 40·51 c.c. at 760 m.m., and 0°C. = ·05064 gramme.

·2725 gramme yielded therefore ·05064 gramme of nitrogen or 18·59 per cent.

		Theory.	I.	II.	III.
C_8	= 48	= 15·90	16·03	15·89	—
H_6	= 6	= 1·98	2·11	2.12	—
N_4	= 56	= 18·55	—	—	18·59
O_{24}	= 192	= 63·57	—	—	—
	302	100·00			

The erythroglucin was reproduced from the nitro-compound by dissolving it in alcohol nearly saturated with ammonia, and passing sulphuretted hydrogen through the solution for some time. After allowing it to stand for about twenty-four hours, the treatment with sulphuretted hydrogen was repeated; a large quantity of sulphur deposited, and after standing some time, the alcohol was removed by distillation, the residue completely extracted by boiling water, and the solution filtered. The filtrate was treated with animal charcoal, and then allowed to evaporate spontaneously. The crystals obtained were pressed between folds of bibulous paper and dissolved in a small quantity of water. After some weeks, large well-characterized crystals of erythroglucin were deposited, together with a few tufts of needles.

XXXVII.—*Note on some Metamorphoses of Oxalic Acid.*

By Arthur H. Church, B.A.

When oxalate of sodium is submitted to the action of sodium-amalgam in presence of water, some interesting effects ensue. If the action be not accelerated by elevation of temperature, and the amount of salt employed be large, a partial reduction only of the oxalic acid takes place, in accordance with the equation—

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} + H_2 = \underset{\text{Glyoxylic acid.}}{C_2H_4O_4}$$

A more ready method of attaining the same result is found in the reaction of zinc, oxalate of zinc, and sulphuric acid. A large quantity of oxalate of zinc is placed, together with a few pieces of pure zinc, in a beaker, the mixture covered with water, and dilute sulphuric acid added very slowly, drop by drop. Milk of lime, in very slight excess, having been added, together with much water, and the mixture warmed, the whole was filtered, saturated with carbonic acid, again warmed, and filtered. The filtrate deposited, on cooling, some quantity of fine needle-shaped crystals of glyoxylate of calcium. This salt required about 160 parts of cold water for solution. Calcium and water determinations suggested for this salt the formula

$$C_2HCaO_3.H_2O,$$

while a series of careful qualitative experiments proved the identity of the acid of which it was the calcium-compound with Debus' glyoxylic acid. A larger yield of this product is obtained if, in the process just given, the use of lime be altogether omitted, the glyoxylic acid being extracted directly by means of ether from the concentrated and acidified solution of the mixed zinc-salts first formed. The syrupy ethereal solution is treated with carbonate of calcium, and the various calcium-salts thus made are separated by the method of Debus.

When lime-water was added to the solution of the glyoxylate, a white powder fell, agreeing in its amount of calcium with the formula

$$C_2Ca_2O_3,$$

and suffering, when boiled for some time with water, the following change—

$$\underset{\text{Glyoxylic acid.}}{2C_2H_2O_3} + H_2O = \underset{\text{Oxalic acid.}}{C_2H_2O_4} + \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

This transformation of oxalic acid into glycollic acid has however been previously accomplished. Under the name of *oxonic* acid, F. Schulze has described one of the products obtained by acting upon oxalic acid with zinc in presence of sulphuric acid. Schulze, indeed, in all probability, thus obtained glyoxylic acid; but his method of eliminating the new product of the reaction, by ebullition of the zinc-salts with excess of milk of lime, necessarily destroyed the glyoxylate first formed, producing oxalate and glycollate, as stated above. But if we adopt Schulze's plan, and instead of moderating in every way the reducing action in the experiment under review, we exalt its energy in every way, then glycollic acid is the chief product. The method of procedure in this case may be thus modified:—Into a retort containing a large quantity of zinc and dilute sulphuric acid, and heated by a lamp, small quantities of oxalic acid are introduced from time to time. When the desired quantity of acid has been added, a brisk evolution of hydrogen is maintained for some hours, and the liquid boiled with excess of zinc till the acids present are saturated. Excess of slaked lime having been added to the mixed salts, the whole is to be saturated with carbonic acid, boiled, and filtered. This filtrate, on concentration, deposits abundance of glycollate of calcium, in concentric tufts of fine crystals. Analysis and qualitative experiments confirmed the identity of the formula of this salt—

$$C_2H_3CaO_3 + \text{aq.}$$

But in the mother liquor from which the glycollate had been deposited, another calcium-salt was contained. This salt was excessively soluble in water, thus differing from the oxalate, the glyoxylate, and the glycollate of calcium. When to its warm syrupy solution an exactly equivalent quantity of sulphuric acid was added, and the sulphate of calcium separated, star-shaped clusters of crystals filled the filtrate. Further examination proved these crystals to be an acid. As far as the small quantity of this substance at my disposal permitted, I have determined some of its properties and its probable composition.

The acid is soluble in water, and readily crystallizable. From

its boiling aqueous solution, it evaporates slowly, with a peculiar faint odour. It melts above 100°C. Its lime salt (the only one yet made) is very soluble in cold water, and confusedly crystalline. A combustion of this acid dried over sulphuric acid indicated the formula

$$C_2H_4O_2;$$

while a calcium determination in the salt of that metal gave numbers nearly agreeing with the formula

$$C_2H_3CaO_2 + aq.$$

If the preliminary examination of these substances has conducted me to a correct conclusion, and I am right in supposing the last-mentioned acid to have the formula assigned to it, we have a new isomer of acetic acid, differing remarkably from that body in several particulars. The series of reduction-products of oxalic acid will stand thus:

Oxalic acid	..	=	$C_2H_2O_4$, which $-$ O gives
Glyoxylic acid	..	=	$C_2H_2O_3$, which $+$ H_2 gives
Glycollic acid	..	=	$C_2H_4O_3$, which $-$ O gives
New acid	..		$C_2H_4O_2$.

By addition of H_2 to the last term, glycol, $C_2H_6O_2$, might perhaps be formed.

The existence of a body $C_2H_4O_2$ has, I find, been predicted by Prof. Kekulé. He gives the following table (*Lehrbuch der Organischen Chemie*, Bd. ii, s. 18)—

Monatomic series:—

C_2H_6O	$C_2H_4O_2$	C_2H_4O
Alcohol.	Acetic acid.	Aldehyde.

Biatomic series:—

$C_2H_6O_2$	$C_2H_4O_3$	$C_2H_2O_4$
Glycol.	Glycollic acid.	Oxalic acid.
$C_2H_4O_2$	$C_2H_2O_3$	$C_2H_2O_2$
(Unknown.)	Glyoxylic acid.	Glyoxal.

It is thus clearly shown how a monatomic alcohol, losing H_2, yields one aldehyde, and this, gaining O, yields one acid; while, on the other hand, a triatomic alcohol, by losing H_2 or $2H_2$ yields two aldehydes, and each of these, by gaining O, yields another acid.

The new acid may thus be the missing first aldehyde of glycol, of which glyoxylic acid may be regarded as the second.

It will not be unreasonable to expect corresponding results from the action of nascent hydrogen on the homologues and analogues of oxalic acid, and the acid and neutral ethers* of these acids.

I have commenced a few experiments in this direction also.

Succinic acid, after the prolonged and energetic action of nascent hydrogen, as above described in the case of oxalic acid, suffers a similar change. I have not endeavoured to moderate the action so as to form the intermediate or butyloxylic acid, but have pushed it to the extreme, so that butylactic acid might be obtained.

The operation was performed in a retort; towards its conclusion a powerful odour, resembling that of butyric acid, was noticed in the aqueous distillate. The mixture of zinc-salts in the retort was evaporated, sulphuric acid added in excess, and the liquid shaken up with ether. From this ethereal solution (besides some unchanged succinic acid) a deliquescent acid was obtained, the properties and salts of which agreed completely with those of the butylactic acid of Wurtz. I have likewise submitted suberic and phthalic acids to the above-described treatment, and the reactions promise interesting results. But the products of these reactions, obtained only within the last few hours, await further purification and analysis; and it would be altogether premature to express any opinion as to their composition.

XXXVIII.—*On the Quantitative Determination of Phosphoric Acid by Salts of Magnesia.*

By Robert Warington, Junr., Assistant in the Laboratory of the Royal Agricultural College, Cirencester.

Phosphoric acid is continually found in nature associated with oxide of iron, and also with alumina. It is in this state of com-

* From oxalate of ethyl M. Löwig has already obtained in this way, paratartaric acid.

bination that we meet with it in soils, coprolites, and other phosphatic minerals, and also in most animal and vegetable products. The accurate determination of phosphoric acid in the presence of iron and alumina is, therefore, a problem of frequent occurrence; and, from its bearings on agricultural economy, of considerable importance.

A method of analysis frequently followed in such cases is first to separate the silica by the ordinary process, next to precipitate the lime by oxalate of ammonia from a solution feebly acid with oxalic or acetic acid, then to concentrate the filtrate, treat with tartaric acid, and finally to add a salt of magnesia and an excess of ammonia. If the tartaric acid has been used in sufficient quantity, the oxide of iron and alumina are held perfectly in solution, while the whole of the phosphoric acid is precipitated as ammonio-phosphate of magnesia.

This process would seem at first sight to include all that could be required. It really, however, involves a considerable source of error, inasmuch as it is found that, under certain circumstances, as mentioned to me by Dr. Voelcker, a tartrate of magnesia is precipitated together with the ammonio-phosphate. According to H. Rose,* indeed, magnesia-salts, mixed with tartaric acid, are *not* precipitated by ammonia. Experiment shows, however, that this is true only when the materials are employed in certain proportions, and not universally. Thus if we take a mixed solution of chloride of magnesium and chloride of ammonium, render it strongly ammoniacal (the ammoniacal salt being present in just sufficient quantity to prevent the precipitation of the magnesia), and then add a small portion of tartaric acid, we obtain in a short time a considerable precipitate of tartrate of magnesia. If, however, instead of adding a *little* tartaric acid, a large quantity is employed, the solution, though made as ammoniacal as at first, remains perfectly clear. This reaction appears at first sight somewhat anomalous. The explanation seems to lie in the fact that the tartrate of magnesia thus formed is completely soluble in salts of ammonia, and among others in tartrate of ammonia. That this is really the case may be shown by adding a larger amount of chloride of ammonium to the magnesian solution, which will be found to prevent any pecipitate being formed, quite as well as a larger quantity of tartaric acid.

* Gmelin, Cavend. Soc. Ed., vol. x, p. 290.

The precipitate of tartrate of magnesia closely resembles the ammonio-phosphate in appearance. It forms slowly, is white and crystalline, remains long in suspension, and deposits a hard crystalline crust on the sides of the vessel. It is sparingly soluble in weak ammonia, and dissolves readily in a boiling solution of chloride of ammonium. I have not yet had an opportunity of determining with precision the exact constitution of this tartrate. Approximate determinations of the magnesia contained in it seem to indicate that it consists of three or four equivalents of base to one of acid. The further analysis of the substance may, therefore, possess some interest.

The amount of error likely to arise in the determinations of phosphoric acid, from the formation of this tartrate of magnesia, will depend, of course, upon the proportion of ammoniacal salts necessary to ensure its perfect solution. The results of various experiments on this point showed that, while this proportion varied considerably according to the state of dilution and the amount of free ammonia present, yet that the conditions under which a precipitate would be formed were, on the whole, by no means unlikely to occur in the ordinary method of determining phosphoric acid. These conditions being (1) the use of a considerable excess of magnesia-salt, (2) a dilute state of the solution, or (3) the presence of much free ammonia; all of which might very likely be found in actual practice.

Under these circumstances it occurred to me that as *citric acid* was equally capable, with tartaric acid, of preventing the precipitation of oxide of iron and alumina, it might be well to try *its* behaviour with magnesia. Some experiments were, therefore, undertaken to this end, and with complete success. Various proportions of the solutions of chloride of magnesium, citric acid, and ammonia, were mixed together, but in no case was there the slightest indication of any precipitate being formed. Here then is an easy solution of the difficulty. We have but to substitute citric acid for the tartaric acid usually recommended, and the source of error is at once removed, and there is no longer any ground for fear lest the precipitate of ammonio-phosphate of magnesia should be contaminated with another salt. Citric acid will be found more especially useful in small operations, as the conditions favourable to the precipitation of the tartrate of magnesia are then most frequently present.

It is scarcely necessary to add that when either citric or tar-

taric acid is used to prevent the precipitation of oxide of iron, such a quantity must be employed that the solution when made ammoniacal shall be of a somewhat greenish "lemon tint." If less acid has been added, and the solution is yellow, orange, or of a reddish colour, the magnesia precipitate will be perceptibly contaminated with oxide of iron.

XXXIX.—*On the Products of the Oxidation of β Hexylic Alcohol.*

By J. A. Wanklyn and E. Erlenmeyer.

When β hexylic alcohol is oxidized with bichromate of potash and dilute sulphuric acid, it yields β hexylic aldehyde, according to the equation—

$$\beta\,C_6H_{14}O - H_2 = \beta\,C_6H_{12}O;$$

but, on pushing the action further, the next product is not caproic acid. Instead of simply taking up another atom of oxygen, the aldehyde falls in pieces when it is treated with more oxygen, and thus, in the second stage of oxidation, the products are butyric acid, water, and carbonic acid.

β Hexylic aldehyde. Butyric acid.

$$\overbrace{C_6H_{12}O} + O_7 = \overbrace{C_4H_8O_2} + 2H_2O + 2CO_2.$$

From this remarkable decomposition we see that two atoms of carbon in the β aldehyde and β alcohol are less firmly bound together than the remaining four carbon atoms. We might then express the difference between the β series and the ordinary or α series, by joining the carbon atoms differently in the two series.

We infer from this strange splitting up which the abnormal alcohol shows, that the difference between the normal and the abnormal series lies deeper than M. Wurtz seems to believe. In addition to β iodide, β alcohol, β aldehyde, and β ether, we think there is a β olefine and a β hydride.

We subjoin an account of β hexylic aldehyde, and of our experiments on the oxidation of β hexylic alcohol.

β Hexylic Aldehyde
$\beta\,C_6H_{12}O$.

Preparation:—Bichromate of potash and dilute sulphuric acid are

heated in a retort, and β hexylic alcohol* is added by small portions at a time. The reaction is brisk, and an oily liquid of a sharp penetrating smell distils over. This distillate, which is the aldehyde, should be again distilled with bichromate of potash and dilute sulphuric acid. It may then be shaken up with aqueous solution of potash and dried with carbonate of potash.

Properties:—β $C_6H_{12}O$ has the penetrating fragrant smell which is characteristic of the aldehydes. It boils quite constantly at 127°C. (bar. = 761·2 mm.)

Its specific gravity at 0°C = ·8298
„ „ 50°C = ·7846

whence the expansion-coefficient for 50°C. = ·0576.

It forms a solid compound with bisulphite of soda, and this compound is decomposed by boiling with water, the aldehyde being separated.

It does not reduce ammonio-nitrate of silver, and seems to have little or no tendency to take up oxygen from the air.

It is not easily (perhaps cannot be) transformed into an alcohol by the action of sodium-amalgam. The experiment was made in the presence of some ethylic alcohol, which would act as a solvent, but no transformation was effected.

Finally it is abnormal: for when oxidized it yields no caproic acid, but is broken up into carbonic acid, water, and butyric acid.

Analyses of it have furnished the following numbers:—

I. ·2956 grm. burnt with oxide of copper, a little chlorate of potassium being used, gave ·7770 grm. CO_2 and ·3229 grm. H_2O.

II. ·2896 grm. similarly treated gave ·7608 grm. CO_2 and ·3230 grm. H_2O.

III. 2888 grm. similarly treated gave ·7572 grm. CO_2 and ·3184 grm. H_2O.

Calculated.		Found.		
		I.	II.	III.
C_6	72	71·69	71·65	71·51
H_{12}	12	12·14	12·39	12·25
O	16	—	—	—
	100			

* The β $C_6H_{14}O$ which we used was obtained from C_6H_{12} (prepared from mannite) by hydrating it by means of sulphuric acid. (See Chem. Soc. J., July, 1863.)

Notes of the experiments on the Oxidation of β $C_6H_{14}O$.

9·5 cub. cent. of β $C_6H_{14}O$ were added by degrees to a heated mixture of 14 grms. bichromate of potash, 27 grms. sulphuric acid, and 20 grms. water. The reaction was very brisk, and a mixed distillate of oil and water came over. The distillate was shaken up with solution of potash, and the oily part (β $C_6H_{12}O$) put back into the retort and distilled over again along with the bichromate of potash, &c. This was repeated several times, and finally the distillate, supersaturated with potash, was evaporated in the water-bath. The concentrated residue was then distilled with sulphuric acid. The distillate was redistilled. It was then very acid, but free from sulphuric and hydrochloric acids. Ammonia was added to it and then solution of nitrate of silver, which determined an abundant white precipitate of silver-salt. The silver-salt having been washed, a small portion dried in the water-bath gave 56·73 per cent. of silver.

The rest of the silver-salt was then treated with dilute nitric acid and again washed. It was dried in the water-bath and analysed.

I. ·1376 grm. gave on ignition ·0775 grm. silver ∴ silver % = 56·32.

II. ·1516 grm. burnt with oxide of copper, a little chlorate of potash being used, gave ·1323 grm. CO_2 and ·0523 grm. H_2O.

This agrees with the composition of butyrate of silver:—

	Calculated.		Found.
C_4	48	24·62	23·80
H_7	7	3·59	3·83
Ag	108	55·38	56·32
O_2	32	16·41	—
	195	100·00	

The theoretical percentage of silver in caproate of silver is 48·4 which is nearly 8 less than that which we find in our silver-salt. If the details which we have given be considered, it will be apparent that if any caproic acid had been formed at the beginning of the oxidation, we should have got hold of it; and inasmuch as caproate of silver is less soluble than its lower homologues, the prolonged

washing of the silver-salt should have favoured the accumulation of caproate in the latter portion of silver-salt whose analysis we have just given. The experiment was repeated.

7·5 grm. of bichromate
15 cub. c. of sulphuric acid
30 cub. c. of water
3·5 cub. c. of hexylic alcohol

were taken. The oxidation soon stopped, when the oily distillate measured 2 cub. c., and it was necessary to take a fresh mixture of bichromate of potash, &c., in the same proportions as just given. An acid was finally obtained which was converted into a silver-salt—

·2206 grm. of the silver salt gave ·1237 grm. of silver.

Silver per cent. = 56·07, which confirms the result of the first experiment.

In a third experiment the formation of large quantities of carbonic acid during the oxidation was proved.

From all this we infer that when $\beta\ C_6H_{14}O$ is oxidized with bichromate of potash and dilute sulphuric acid, the first stage of the reaction is—

$$C_6H_{14}O + O = C_6H_{12}O + H_2O;$$

and the second—

$$C_6H_{12}O + O_7 = C_4H_8O_2 + 2H_2O + 2CO_2.$$

XL.—*On Larixinic Acid, a crystallisable principle found in the Bark of the Larch Tree* (Pinus Larix, *Linn.*)

By Dr. John Stenhouse, F.R.S.

(From the Philosophical Transactions, 1863, p. 53.)

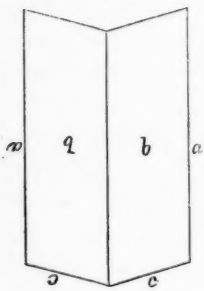
The most convenient way of preparing this somewhat singular substance consists in cutting the bark of the larch into small pieces, and then digesting it in water for twenty-four hours at a temperature of about 80° C. The solution, which has a deep reddish-brown colour, is then poured off on to a second portion of

larch bark and digested as before. The concentrated infusion is then cautiously heated in an open porcelain dish, at the temperature of about 80° C., till it is converted into a syrup. A portion of this syrup is then distilled, either in glass or porcelain retorts, or, what is better than either, in a silver alembic. Iron retorts cannot be employed for this purpose, as the acetic acid which is always produced during distillation, by forming acetate of iron, instantly destroys the larixinic acid, changing it into a deep-purple-coloured liquid. When a silver alembic cannot be procured, a very convenient way of distilling the extract of the larch is to pour it into a large Florence flask, the neck of which is passed obliquely through a cork or bung, inserted into a glass condenser. When the flask is cautiously heated on a sand-bath, the larixinic acid comes over with the first portions of the liquid, but becomes more abundant as the distillation proceeds, and usually forms large flat crystals which condense on the sides and neck of the receiver. The liquid which is distilled over, and which contains the greater portion of the larixinic acid, should be poured into small flat basins, and cautiously concentrated at about 60° C. When the greater portion of the water has been dissipated, it is advisable, especially in warm weather, to complete the operation by spontaneous evaporation; for unless the concentration of the aqueous solution of larixinic acid is conducted cautiously, the larixinic acid volatilizes along with the vapour of water, and is thereby lost. The highly concentrated solution of larixinic acid obtained in the way just described, desposits, on standing, brownish-yellow crystals, which are impure larixinic acid. This is to be pressed between folds of blotting-paper, and recrystallised from a small quantity of water. The larixinic acid may be rendered perfectly pure by subliming it once or twice. This is easily effected by placing the larixinic acid between two watch-glasses, or in any other suitable apparatus, and heating it cautiously on a sand-bath, or even on a water-bath, as it sublimes at the very low temperature of 93° C. The larixinic acid is a proximate principle, which exists ready formed in the larch. This is easily proved by distilling even a dilute infusion of the bark, when the liquid which passes over will be found to strike a deep purple colour with a persalt of iron, which is very persistent. The bark of old larch trees contains very little larixinic acid; but the bark of the small branches, and that of the stems of the larch, when not more than from twenty

to thirty years of age, contains very considerable quantities of this substance, the concentrated syrup from the portions of bark yielding more larixinic acid than an equal weight of catechu does of oxyphenic acid. Larixinic acid, after it has been purified by sublimation, forms beautifully white crystals, often more than an inch in length, of a brilliant silvery lustre, very much resembling benzoic acid in appearance. They sublime at 93° C., and melt at 153° C., but the aqueous solutions volatilize at ordinary temperatures. I am indebted to the kindness of Professor W. H. Miller, of Cambridge, for the subjoined measurements of the crystals of larixinic acid.

"The crystals obtained by sublimation become rough so rapidly when exposed to the air, that very little confidence can be placed in the following results:—

Fig. 1.



"The crystals belong to the oblique system; they usually occur in twins, like the annexed figure. They are extremely thin in a direction perpendicular to *b*. Denoting by *l*, *m*, *n* faces in the zone *a b*, and by *r* a face in the zone *b c*, it appears that tan *b l*, tan *b m*, tan *b n* are nearly as the numbers 2, 3, 6, and that $a\ b = 90° 0'$, $b\ c = 90° 0'$, $a\ c = 76° 0'$, $b\ l = 49° 29'$, $b\ m = 60° 20'$, $b\ n = 74° 6'$, $b\ r = 75° 30'$. Cleavage *a* distinct, *c* imperfect.

"The crystals of larixinic acid crystallised from water are very imperfect; the angles must be regarded as very rough approximations. They are deduced, as well as I could deduce them, from a mean of a considerable number of observations by no means agreeing with each other. The angle between the normals to two faces is taken as the measure of the angle between the faces.

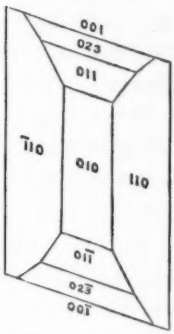
"Oblique:—

$1\,0\,0,\ 1\,0\,1 = 26° 22'$
$0\,1\,0,\ 1\,1\,1 = 74° 36';\ 0\,0\,1,\ 1\,0\,1 = 44° 20'.$

"Forms observed:—

0 1 0, 0 0 1, 1 1 0, 0 1 1, 0 2 3.

Fig. 2.



Angles.

1 1 0, 0 0 1	=	71° 58′
1 0 1, 1 1 0	=	69° 35′
0 1 0, 0 1 1	=	59° 37′
0 1 0, 0 2 3	=	68° 39′
0 1 0, 0 0 1	=	90° 0

"Cleavage 0 0 1 distinct, and very easily obtained."

The smell of the aqueous solution of larixinic acid is sweetish, like that of a syrup, but the smell of the sublimed acid is very peculiar and slightly empyreumatic. As larixinic acid emits a sensible odour at ordinary temperatures, it bears in this respect a considerable resemblance to naphthaline and ordinary camphor. The taste of larixinic acid is slightly bitter and astringent. It reddens litmus paper very slightly, but a single drop of potash or ammonia, when added to a solution of a large quantity of larixinic acid, renders it alkaline. Larixinic acid is very soluble in boiling water, but by no means very soluble in cold water, 87·88 parts of water at 15° C. dissolving 1 part of the acid only; but the solubility of larixinic acid in cold aqueous solutions is greatly increased by the addition of either acids or alkalies. Larixinic acid is deposited from its aqueous solutions in crystals which are very brittle, and often an inch or two in length. It likewise dissolves in cold alcohol, but to a much greater extent in hot alcohol. The crystals deposited from its alcoholic solutions are thicker and more distinctly formed than those from water. It also dissolves but sparingly in ether, and is deposited in crystals of very considerable lustre.* The following are the results of the analysis of the larixinic acid:—

	Calculated Numbers.	Found.		
		I.	II.	III.
C_{20}	= 57·14	57·13	57·06	57·09
H_{10}	= 4·77	5·04	5·09	5·04
O_{10}	= 38·09	37·83	37·85	37·87

* The crystals of larixinic acid catch fire readily, and burn with a bright flame, leaving no residue.

From these results it is evident that the carbon, hydrogen and oxygen in larixinic acid are in the proportion of $C_2H_1O_1$, or some multiple of these numbers, $C_{20}H_{10}O_{10}$ being the numbers we have adopted as the more probable.

When a quantity of larixinic acid was dissolved in a great excess of liquid ammonia, a yellow-coloured solution was produced; when this was evaporated to dryness over sulphuric acid *in vacuo*, the larixinic acid was deposited in crystals which were nearly unaltered. It gave its characteristic reactions with salts of iron, and when boiled with milk of lime gave off no trace of ammonia. The combination which larixinic acid forms with ammonia is, therefore, so feeble, that it is decomposed by the volatility of the ammonia. In this respect, therefore, and in its forming no hydrate, larixinic acid closely resembles both pyrogallic and oxyphenic acids.

When larixinic acid was treated with an excess of aqua potassæ it very readily dissolved, forming a yellowish solution. When dried over sulphuric acid *in vacuo*, the potash combination formed long flattish crystals having considerable lustre, but of a reddish-brown colour. These crystals, when pressed between folds of blotting-paper to free them from excess of potash, and recrystallised *in vacuo*, yielded crystals which were more deeply coloured than the first. This potash combination is so very feeble that it is decomposed by carbonic acid. It contained a considerable quantity of potash; but I have not been able to obtain it of a constant composition.

A solution of larixinic acid gives no precipitate, either with lime-water or with saccharate of lime. The behaviour of larixinic acid with baryta is extremely singular and characteristic. When a solution of caustic baryta is added to a concentrated aqueous solution of larixinic acid, the latter being in excess, a bulky semi-transparent, gelatinous precipitate immediately falls, and if the solutions are concentrated, fills the whole vessel. This precipitate, which considerably resembles hydrated alumina, is but slightly soluble in cold water; but it dissolves very readily in boiling water, from which it is again deposited on the cooling of the liquid. This baryta-compound is readily decomposed by carbonic acid. When thrown on a filter and washed, the air being carefully excluded, it was dried *in vacuo* over sulphuric acid, and was then found to contain, as the mean of two experiments, 34·92 per cent. of baryta.

A solution of larixinic acid yields no precipitate with either

basic or neutral acetate of lead, neither is it precipitated by nitrate or ammonio-nitrate of silver; but when its solution in the latter salt is boiled, the silver is reduced in a pulverulent state. Larixinic acid forms no precipitate with perchloride of platinum, even on the application of heat. It does not contain any nitrogen. It does not reduce oxide of copper when tried by Trommer's test. It dissolves in concentrated sulphuric acid, but no conjugate combination is produced, as was ascertained by neutralizing with carbonate of baryta, larixinic acid being obtained unchanged. When larixinic acid is boiled with a mixture of hydrochloric acid and chlorate of potassa, it is decomposed, but without the formation of chloranile. When it is boiled with a solution of hypochlorite of lime, no coloration is produced. It is readily attacked by nitric acid, especially when assisted by heat; nitrous fumes are given off, and oxalic acid is the only fixed product. It is also readily attacked by bromine, especially when assisted by heat. Abundant vapours of hydrobromic acid are given off, the larixinic acid being entirely destroyed and converted into an uncrystallisable resin. The salts of copper produce an emerald-green colour in solutions of larixinic acid, but no precipitate. Chloride of manganese produces neither coloration nor precipitation. Protosulphate of iron strikes a brownish-red colour with solutions of larixinic acid, which acquire a brighter red colour on standing, resembling meconate of iron. Perchloride and persulphate of iron produce a beautiful purple dahlia-colour, which is very persistent, and stands dilution well. Its reactions with salts of iron are very characteristic of larixinic acid, which forms an excellent reagent for the detection of salts of iron, even in very minute quantities. In this way the presence of iron in tolerably pure sulphate of copper can readily be detected by the purple coloration produced. Larixinic acid does not affect neutral protonitrate of mercury in the cold; and on the application of heat no mercury is reduced.

Larixinic acid appears to be peculiar to the larch tree; at least I have not been able to find a trace of it in the bark of the spruce fir *(Abies excelsa)*, or in that of the Scotch fir *(Pinus sylvestris)*. Larixinic acid evidently belongs to that small group of substances of which pyrogallic acid and pyrocatechin, the oxyphenic acid of Gerhardt, are the only other members yet known. Larixinic acid is much less easily oxidisable than oxyphenic acid, which again is less easily oxidated than pyrogallic acid. Larixinic acid volatilises at a much lower temperature than either of these two

substances, from which it also differs in being a ready-formed proximate principle, and not an educt.

Addendum.—In consequence of the extremely feeble, if not somewhat doubtful, acid properties of the so-called larixinic acid, perhaps the name *Larixin* would be more appropriate; but in that case the name of pyrogallic acid should be altered to *pyrogallin*, and that of oxyphenic acid to *pyrocatechin*, the name originally given to it by Zwenger.—J. S.

XLI.—*On the Oxidation and Disoxidation effected by the Alkaline Peroxides.*

By B. C. Sir Brodie, F.R.S., Professor of Chemistry in the University of Oxford.

[From the Philosophical Transactions, 1863, p. 837.]

In a former paper* I communicated to the Royal Society the results of an enquiry as to the cause of the mutual decomposition which takes place between the alkaline peroxides and the oxides of the less electro-positive metals. This decomposition, the first instance of which was discovered by Thénard in the case of the peroxide of hydrogen, had been regarded as of an exceptional and abnormal character, and as such had attracted the attention of chemists, and been accounted for by several hypotheses.

These explanations, which attempted to show that the phenomena were caused by the repulsion of particles similarly electrified, or were the consequence of the laws of mechanical vibration, assumed their abnormal character, and tended to isolate them from other chemical changes, rather than to comprehend them under the same laws.

In the paper referred to I ventured to suggest that this mode of viewing these decompositions was erroneous, that the phenomena were of a normal character, and were to be regarded as a particular case of those general laws under which all chemical changes are included. On the views there developed, every chemical change is considered as determined by the mutual attraction of particles, or groups of particles, in opposite polar conditions.

* See Philosophical Transactions, 1850, Part II. p. 759.

No *à priori* presumption can be raised that certain particles are susceptible of this polarization, and others not; this point can be determined by experiment alone: and I brought forward several examples, the applicability of which is now very generally admitted, in illustration of the point that the elemental bodies, at the moment of chemical change, exhibit the same phenomena of polarization, and are subject to the same laws of diæresis and synthesis as all other chemical substances. On these ideas, as we regard the weight of two volumes of oxygen, that is to say the weight of a molecule of oxygen, O_2, as differing from the weight of two volumes, that is, the weight of a molecule of water, H_2O, in the fact that this weight contains 16 parts of oxygen in the place of two of hydrogen, so do we regard the event of the synthesis or diæresis of oxygen as differing from the event of the synthesis or diæresis of water, in the fact that in the one change the two atoms of oxygen fulfil the same functions, and are respectively in the same polar conditions as the two atoms of hydrogen and the one atom of oxygen in the other.

This theory is of a purely relative character; it is connected with no special hypothesis as to the nature of oxygen or water, but it states that, if we make a certain assertion as to the molecular nature of water, we must, in consistency, make certain parallel assertions as to the molecular nature of oxygen. Our molecular hypotheses may change, but this relation will still remain.

Views as to the polarization of oxygen, and the cause of the decompositions effected by the alkaline peroxides, which, to a great extent, are identical with the preceding, and in which the same language and the same notation are employed, have recently been put forward, with considerable pretension, as new and originating with himself, by Schönbein, Professor of Chemistry at Basle.* This chemist can scarcely be aware of the memoir referred to, as in his numerous publications he makes no allusion to it. A reclamation of a priority of ten years ought not to be required, but I am compelled to call the attention of chemists to these circumstances, in order that I myself may not be considered to appropriate without acknowledgment the ideas and discoveries of another.

* See Annalen der Chemie, vol. cviii. p. 157, Schönbein, "Ueber die gegenseitige Katalyse einer Reihe von Oxyden, Superoxyden und Sauerstoffsäuren, &c." Also see Phil. Mag. [4.] xvi. p. 178, "Further Observations on the Allotropic Modifications of Oxygen, &c."

The decomposition of the alkaline peroxides by the oxide of silver, and other similar bodies, is complicated by the circumstance that not only is the peroxide decomposed by the metallic oxide, but the reduced silver, which is a necessary product of the action, and also probably the oxide of silver itself, is capable of decomposing the peroxide by that continuous form of action which is spoken of as Catalytic. This interferes with the result; the amount of oxygen evolved depends upon the relative velocity with which these two forms of decomposition occur; and while the reduction in equal atomic proportions is never exceeded, and by certain modifications of the experiment may be very closely approximated to, it yet is never absolutely realized, for the catalytic action cannot be entirely eliminated. So that the total loss of oxygen from the oxide of silver in the experiment represents the relation which subsists between these two forms of decomposition, simultaneously occurring, and varies between the limits of the infinite, or catalytic action on the one hand, and the reduction in atomic proportions on the other.

That this is the true account of the phenomena is seen from the fact that, where these disturbing causes do not exist, the decomposition takes place in simple atomic proportions. This was shown to be the case in the decomposition of the peroxide of barium by iodine in the presence of water. The final result of this action is expressed by the equation

$$I_2 + Ba_2O_2 = 2BaI + O_2.$$

It may be considered as taking place by the decomposition and re-formation of water, according to the two equations,

$$I_2 + Ba_2O_2 + H_2O = 2HI + Ba_2O + O_2,$$
$$2HI + Ba_2O = 2BaI + H_2O.$$

The parallel character of this reaction to that of the reduction of the metallic oxide is sufficiently evident. Nevertheless, it was desirable absolutely to realize the normal change in the case of the oxide itself, and to discover a case in which the catalytic action should be eliminated.

In the paper referred to I gave several examples of the decomposition of the alkaline peroxides, effected by the action of oxidizing substances in aqueous solution—such, for example, as the

decomposition of the peroxide of hydrogen by chlorine and by permanganic acid, and of the peroxide of barium by the alkaline hypochlorites and by a solution of ferricyanide of potassium. These reactions are free from the complicating circumstances before mentioned. The present paper contains an investigation of several of these decompositions; it will be seen that they follow the normal law of chemical action, that is, the two substances which enter into the change are decomposed in a simple atomic ratio, and that these decompositions differ from other chemical changes in no single respect, and need, to account for them, no special hypothesis.

The experiment discovered by Barreswil, of the reduction of the peroxide of hydrogen by chromic acid, presents points of special interest. We have in this case an action varying with the proportion present of the decomposing substances, and apparently of an abnormal character, which, however, is shown by accurate investigation to be subject to the atomic law, and to be capable of being broken up into two simple reactions.

From the effects of reduction I proceed to consider the effects of oxidation produced by the alkaline peroxides, which are of considerable theoretical importance. Certain theories have been formed as to the different nature of the oxygen in the different classes of peroxides, based on a supposed difference in the properties of this oxygen. It will be shown that the difference of properties, to account for which these hypotheses have been invented, does not exist, and that, by suitable modification of the circumstances of the experiment, the results of oxidation produced by the peroxide of manganese may equally be realised by the peroxide of barium.

Lastly, I shall give some experiments on the catalytic decomposition which this class of peroxides undergoes, instituted with the view of discovering the cause of this action, and the way in which these phenomena are connected with the ascertained properties of the peroxides. This form of decomposition I believe to be the consequence of that double function of oxidation and reduction which is peculiar to this group of substances.

In the experiments which follow, which were made by means of standard solutions, the amount of solution employed was measured by the aid of a series of carefully calibrated pipettes, which were so arranged that the capacity of each was an exact multiple of the

capacity of the smallest pipette. The capacity of this pipette, which I shall designate as P, was equal to 4·55 cub. centims. The other pipettes are designated as 2 P, 3 P,...10 P, &c.

The peroxide of barium employed was prepared by precipitation, according to a method elsewhere described. It was free from all impurities, except a trace of carbonate. When a solution of peroxide of hydrogen is spoken of, it is to be understood as the solution of this peroxide of barium in dilute hydrochloric acid.

The solutions of peroxide of sodium were prepared by digestion of the moist and freshly-precipitated hydrate of the peroxide of barium with carbonate of sodium, and filtration from the carbonate of barium formed, or, in some cases, by precipitation of the solution of peroxide of barium in hydrochloric acid by carbonate of sodium, and filtration.

In the numerous experiments and calculations which have been made in the course of the following investigation, and of which a small part only is here recorded, I have been much indebted to the skill and care of my assistant, Mr. F. Schickendanz.

1. *Decomposition of a Solution of Peroxide of Hydrogen by Permanganic Acid.*

When a solution of permanganate of potassium is mixed with an acid solution of the peroxide of hydrogen, a decomposition of both substances ensues, oxygen gas is evolved, and a colourless solution formed containing a protosalt of manganese.

The proportion in which the substances are decomposed in this reaction was determined in the following manner.

A portion of pure peroxide of barium was dissolved in very dilute hydrochloric acid; a measured quantity of this solution was decomposed by hydriodic acid, and the amount of iodine formed estimated with sulphurous acid, according to the mehod of Bunsen.

A measured amount of the solution of permanganate of potassium was decomposed by hydrochloric acid, and the iodine formed estimated by the same method.

A measured amount of the solution of peroxide of hydrogen was decomposed by the solution of permanganate, which was added from the burette until the solution was faintly coloured.

Now, if s be the parts of the standard iodine solution required for the decomposition of 1 cub. centim. of the solution of peroxide

of hydrogen, and if s_1 be the parts of the iodine-solution required for the decomposition of 1 cub. centim. of the solution of permanganate of potassium, where s and s_1 are determined according to the usual formula

$$s = \frac{nt - t_1}{p},$$

and if m be the parts of the solution of peroxide of hydrogen decomposed by the permanganic acid, and m_1 be the parts of the solution of permanganate required to effect their decomposition, and if x be the ratio of the amount of oxygen evolved from the peroxide of hydrogen to the amount of oxygen evolved from the permanganate, then

$$x = \frac{ms}{m_1 s_1}.$$

Two distinct series of experiments gave $x = 1{\cdot}0007$ $x = 0{\cdot}9945$.*

This experiment affords a simple and accurate method of determining by titration with a solution of permanganate the absolute amount of oxygen in a solution of the peroxide of hydrogen.

If e be the amount of oxygen contained in 1 cub. centim. of the permanganate, and y the amount of oxygen in 1 cub. centim. of the peroxide, then

$$y = \frac{m_1}{m} e.$$

The above experiments prove that in this decomposition the decomposing substances evolve equal quantities of oxygen† ; the final result of the change may be thus stated,

$$4HCl + H_2Mn_4O_8 + 5H_2O_2 = 4MnCl + 8H_2O + 5O_2.$$

I have varied this experiment in many ways, by adding the peroxide of hydrogen to the permanganate, and by taking the solutions excessively dilute and excessively concentrated, with the view of eliciting a variation in the reaction, but have constantly obtained one and the same result. Although the above equation expresses accurately the final result of the decomposition, we are not to believe that the five molecules of oxygen are at once eliminated, but rather that

* The numerical details of the experiments are omitted in the present abstract.

† This reaction has also been investigated by Aschoff with the same result.—Répertoire de Chimie pure, vol. iii, p. 296.

the substance passes through five successive stages of disoxidation, very rapidly succeeding one another. If to an excess of an alkaline solution of permanganate an alkaline solution of the peroxide of sodium be added, oxygen is evolved, the solution still remains clear, but becomes of the characteristic green colour of the manganate of potassium. On the addition of a further portion of the alkaline peroxide, oxygen is again evolved, the solution becomes colourless, and hydrated peroxide of manganese is precipitated. If this precipitate be added to an acid solution of the peroxide of hydrogen, oxygen is again evolved, both the peroxides are destroyed, and a solution is formed of a protosalt of manganese, showing the successive formation and reduction of each of the oxides before the final result is attained.

2. *Decomposition of a Solution of Peroxide of Hydrogen by Ferricyanide of Potassium.*

When an acid solution of the peroxide of hydrogen is mixed with an acid solution of ferrocyanide of potassium, an oxidation takes place, and the ferrocyanide passes into ferricyanide of potassium. This action requires time, and takes place with extreme slowness in dilute solutions.

If, on the other hand, an alkaline peroxide be mixed with an alkaline or neutral solution of ferricyanide of potassium, the reverse action takes place, oxygen gas is evolved, and the ferricyanide passes into the ferrocyanide of potassium.

The proportion in which the substances are decomposed in this reaction was thus determined:—

A solution was made of ferricyanide of potassium, of which the value in terms of a standard solution of permanganate of potassium, was ascertained as follows. A measured amount of the solution was converted to ferrocyanide by adding to it a great excess of recently precipitated hydrated peroxide of barium, the solution was boiled until the excess of peroxide of barium was completely decomposed, and the amount of ferrocyanide formed was determined by means of the standard solution of permanganate.*

A measured amount of a solution of peroxide of hydrogen, the value of which had been estimated by the process before described

* This affords an excellent method for the estimation of ferricyanide of potassium.

in terms of the same solution of permanganate, was precipitated by an excess of baryta-water. To this a measured amount of the solution of ferricyanide was gradually added by means of a pipette. After the experiment, the solution was diluted with water and acidulated. The excess of peroxide and the ferrocyanide present was determined by means of the same solution of permanganate.

It is evident that the subsequent addition of permanganate would effect two results,—the decomposition of the excess of peroxide, and the reconversion of the ferrocyanide formed to the condition of ferricyanide.

Since in an acid solution the ferrocyanide is oxidised by the peroxide of hydrogen to ferricyanide, a portion of the ferrocyanide reduced will have undergone that conversion, and an equivalent portion of the peroxide of hydrogen will have disappeared.

Now, puting s = the parts of permanganate solution equivalent to 1 part of the solution of peroxide of hydrogen employed, and s_1 = the parts of permanganate solution equivalent to 1 part of the solution of ferricyanide employed,

and putting m = the parts of the solution of peroxide of hydrogen, and m_1 = the parts of the solution of ferricyanide respectively decomposed,

and if x = the ratio of the oxygen evolved from the peroxide of hydrogen to the oxygen evolved from the solution of ferricyanide, then

$$x = \frac{ms}{m_1 s_1}.$$

The value of ms is thus given :—

Putting n = the parts of the solution of peroxide of hydrogen employed in the experiment, and p = the parts of the solution of permanganate required after the termination of the reaction,

$$ms = ns - p + m_1 s_1,$$

whence

$$x = 1 + \frac{ns - p}{m_1 s_1}.$$

In the second of the following experiments the ferricyanide was taken in excess, in which case

$$n = m, \quad m_1 s_1 = p,$$

and

$$x = \frac{ms}{p}.$$

Both experiments gave $x = 1{\cdot}000$.

The final result of this decomposition is given in the equation

$$2(K_3Fe_2Cy_6) + Ba_2O_2 = 2(K_3BaFe_2Cy_6) + O_2.$$

3. *Decomposition of a Solution of Peroxide of Hydrogen by Hypochlorite of Barium.*

When peroxide of barium is mixed with a solution of an alkaline hypochlorite, oxygen gas is evolved, and both substances are decomposed.

The following experiments were made with the hypochlorite of barium. It was prepared by leading chlorine through a solution of hydrate of barium to complete saturation, the excess of chlorine being afterwards expelled by a current of air.

The amount of hypochlorite of barium present in the solution was estimated by decomposing the solution with hydriodic acid, according to the method of Bunsen.

The value of the solution of peroxide of hydrogen was estimated, as before, with permanganic acid.

When the peroxide of hydrogen was taken in excess, a measured amount of the solution was precipitated by a solution of hydrate of barium. To this a measured amount of the solution of hypochlorite was added by a pipette. After the decomposition, the excess of peroxide of barium was estimated by determination with permanganic acid, the solution being first diluted and rendered acid.

When the hypochlorite was taken in excess, a measured amount of the solution was rendered strongly alkaline with baryta-water, and the measured amount of the solution of peroxide of hydrogen added to this by means of a pipette. The excess of hypochlorite present after the decomposition was estimated by the iodine method.

In the former case, putting

s = the parts of permanganate required to effect the decomposition of 1 part of the peroxide of hydrogen employed,

s_1 = the parts of permanganate equivalent to 1 part of the solution of hypochlorite of barium employed, as calculated from the determination with iodine,

m = the parts of the solution of peroxide decomposed,

m_1 = the parts of the solution of hypochlorite decomposed,

x = the ratio of the amount of oxygen evolved from the peroxide of hydrogen to that evolved from the hypochlorite,

$$x = \frac{ms}{m_1 s_1},$$

where, putting n = the parts of the solution of peroxide employed in the experiment, and p = the parts of permanganate required to decompose the excess of peroxide after the decomposition,

$$ms = ns - p,$$

and

$$x = \frac{ns - p}{m_1 s_1}.$$

In the second case, where the hypochlorite was taken in excess, let

s = the parts of the standard iodine solution equivalent to 1 part of the solution of peroxide of hydrogen;

s_1 = the parts of the same solution equivalent to 1 part of the solution of hypochlorite;

m = the parts of the solution of peroxide employed in the experiment;

m_1 = the parts of the solution of hypochlorite decomposed;

then, as before,

$$x = \frac{ms}{m_1 s_1},$$

where, putting n_1 = the parts of hypochlorite employed in the experiment, and p_1 = the parts of the iodine-solution equivalent to the excess of hypochlorite present, as determined by experiment,

$$m_1 s_1 = n_1 s_1 - p_1,$$

and

$$x = \frac{ms}{n_1 s_1 - p_1}.$$

I. Peroxide of barium in excess. Two experiments gave $x = 0{\cdot}997$ and $x = 0{\cdot}99$.

II. Hypochlorite of barium in excess gave $x = 0{\cdot}999$.

The final result, therefore, of the decomposition is in both cases expressed by the equation

$$BaClO + Ba_2O_2 = BaCl + Ba_2O + O_2.$$

I have ascertained by similar experiments that an equivalent of chlorine in aqueous solution decomposes an equivalent of the peroxide of hydrogen, according to the equation

$$Cl_2 + H_2O_2 = 2HCl + O_2.$$

Decomposition of Chromic Acid by Peroxide of Hydrogen.

The previous reactions are of a normal character. The peroxide of hydrogen, and the permanganic acid, or alkaline hypochlorite, are simultaneously decomposed in simple atomic proportions, and the formation of the oxygen evolved is subject to the general law of atomic combination. The decomposition of the peroxide of hydrogen by chromic acid has a character apparently exceptional, and it is only by an attentive study of the reaction that it is seen to be of the same class as the preceding.

Having ascertained, by preliminary experiments which it is unnecessary to detail, that the quantity of peroxide of hydrogen decomposed by the same quantity of chromic acid was variable in amount, and depended upon the proportion in which the two substances were present, I instituted a series of experiments with the view of determining the law of this action.

The absolute amount of the solution of peroxide of hydrogen employed in each experiment was the same, namely 20 P., or very nearly 100 cub. centims. This solution was made up of three parts; of a standard solution of peroxide of hydrogen, of dilute hydrochloric acid, and of water. It is readily seen how, by means of the system of calibrated pipettes before mentioned, the bulk of this solution could be kept constant, while the amount of peroxide of hydrogen contained in it could be caused to vary. The hydrochloric acid employed was excessively dilute, and the same quantity of acid was used in each experiment. I ascertained, however, that the absolute amount of hydrochloric acid used had, within considerable limits, no appreciable influence on the reaction. Into this solution, which was contained in a small flask, and kept in a state of rapid agitation during the experiment, the solution of chromic acid was allowed to run freely from the pipette in which it was measured. After the first rapid evolution of oxygen had ceased, and the blue colour had disappeared, the solution was allowed to remain for 16 or 18 hours, and the excess of peroxide of hydrogen was then determined in the manner to be described.

In dilute solutions a very considerable time is required for the completion of the reaction.

When the chromic acid was in excess, the experiment was conducted in a precisely similar way, the solution of chromic acid being brought to the standard bulk of 20 P. The result was absolutely the same, whether the peroxide of hydrogen was gradually dropped into the chromic acid, or allowed to run freely from the pipette. On the effects of dilution and temperature I am not yet able to speak with precision; but the solution may at any rate be considerably diluted (for example, mixed with an equal bulk of water) with no appreciable variation in the results.

The value of the solutions of peroxide of hydrogen and of chromic acid employed, was determined by means of the same standard iodine-solution; and the excess present, after the decomposition, of the peroxide of hydrogen or of chromic acid,* was also estimated in the same manner.

Now, putting

s = the parts of the iodine-solution equivalent to 1 part of the solution of peroxide of hydrogen employed;

s_1 = the parts of the same solution equivalent to 1 part of the solution of chromic acid employed;

m = the parts of the solution of peroxide of hydrogen decomposed in the experiment;

m_1 = the parts of the solution of chromic acid decomposed in the same experiment;

x = the ratio of the oxygen evolved from the peroxide of hydrogen to the oxygen evolved from the chromic acid in the same experiment;

then

$$x = \frac{ms}{m_1 s_1}.$$

Also putting

n = the parts of the solution of peroxide of hydrogen employed in the experiment;

n_1 = the parts of the solution of chromic acid employed in the same experiment;

* Chromic acid cannot be accurately estimated by this method if the solution be very dilute. In strong solutions the error is inappreciable, as I have ascertained by direct experiment. Similar difficulties occur if it be attempted to estimate directly a solution of peroxide of hydrogen by a standard solution of sulphurous acid. To ensure an accurate result, the peroxide of hydrogen must be first decomposed by hydriodic acid, and the iodine formed estimated by sulphurous acid.

r = the ratio of the oxygen contained in the peroxide of hydrogen to the oxygen contained in the chromic acid employed in the experiment;
then

$$r = \frac{ns}{n_1 s_1}.$$

This ratio I shall term the ratio of mass.

Further, putting

p = the parts of the iodine-solution equivalent to the excess of peroxide of hydrogen after the completion of the decomposition;

p_1 = the parts of the iodine-solution* equivalent to the excess of chromic acid after the completion of the experiment, as determined by the formula $p = nt - t_1$;
then

$$x = \frac{ms}{m_1 s_1} = \frac{ns - p}{n_1 s_1 - p_1},$$

where either p or $p_1 = 0$, according as the chromic acid or peroxide of hydrogen is in excess.

And if y be the ratio of the difference of the amount of oxygen contained in the peroxide of hydrogen and the amount of oxygen contained in the chromic acid employed, to the amount of oxygen evolved from the chromic acid decomposed, then

$$y = \frac{ns - n_1 s_1}{n_1 s_1 - p_1} = \frac{n_1 s_1}{n_1 s_1 - p_1}.(r - 1).$$

So long as the chromic acid is not in defect, the whole of it being decomposed, $y = r - 1$. If the oxygen in the peroxide of hydrogen be equal to that in the chromic acid employed, $y = 0$; if this oxygen be greater in amount than that in the chromic acid, y is positive; if less, y is negative.

Also

$$\frac{x}{y} = \frac{ns - p}{ns - n_1 s_1}.$$

The numerator of this fraction represents the number of atoms of oxygen evolved from the peroxide of hydrogen; and the denominator the difference of the number of atoms of oxygen con-

* In these experiments, a proportionate part of the solution was titred after the completion of the reaction, and the values of p and p_1 calculated. In strong solutions the error, from this cause, is accumulated and may become considerable. To this may be attributed the deviation from the mean in experiments 1, 3, and 4 of the following Table.

tained in the peroxide of hydrogen, and the number of atoms of oxygen contained in the chromic acid employed in the experiment.

Also if x_1, be the ratio of the total amount of oxygen evolved from the solution, to that evolved from the chromic acid,

$$x_1 = \frac{ns + n_1 s_1 - \overline{p + p}}{n_1 s_1 - p_1} = 1 + x.$$

The proportion of the oxygen evolved to the whole oxygen taken in the experiment

$$= 1 - \frac{p + p_1}{ns + n_1 s_1}.$$

* From the numerical results of the experiments, we obtain the following values for r, y and x:—

	r.	y.	x.	Mean value of y.	Mean value of x.
1.	0·068	− 12·65	0·959	− 12·65	0·975
2.	....	....	0·991		
3.	0·110	− 9·02	1·103	− 9·02	1·113
4.	....	....	1·123		
5.	0·123	− 7·34	1·042	− 7·34	1·038
6.	....	....	1·026		
7.	0·164	− 5·25	1·037	− 5·25	1·037
8.	....	....	1·037		
9.	0·247	− 3·16	1·031	− 3·16	1·037
10.	....	....	1·043		
11.	0·329	− 2·11	1·033	− 2·11	1·035
12.	....	....	1·037		
13.	0·402	− 1·61	1·017	− 1·61	1·014
14.	....	....	1·011		
15.	0·814	− 0·25	1·093	− 0·25	1·103
16.	....	....	1·111		
17.	1·100	0·10	1·001	0·10	1·001
18.	1·223	0·223	1·223	0·222	1·222
19.	1·222	0 222	1·222		
20.	2·444	1·444	1·506		
21.	2·446	1·446	1·462	1·457	1·492
22.	2·480	1·480	1·507		
23.	3·720	2·72	1·696		
24.	3·648	2·648	1·728	2·691	1·709
25.	3·705	2·705	1·703		
26.	4·888	3·888	1·803		
27.	4·864	3·864	1·799	3·876	1·811
28.	....	....	1·833		
29.	6·08	5·08	1·911		
30.	6.16	5·16	8·905	5·15	1·918
31.	6·20	5·20	1·909		

* The Table containing these numerical results is omitted.

	r.	y.	x.	Mean value of y.	Mean value of x.
32.	7·39	6·39	2·034	6·39	2·000
33.	....	....	1·977		
34.	8·554	7·554	2·023	7·647	1·992
35.	8·743	7·74	1·989		
36.	....	....	1·962		
37.	9·993	8·993	2·003	8·993	2·003
38.	....	....	2·003		
39.	11·24	10·24	2·032	10·24	2·027
40.	....	....	2·022		
41.	21·816	20·816	2·079	20·816	2·061
42.	....	....	2·043		

A graphic delineation of the results is given in the curve annexed, Plate XXXVII.

It will be observed, on inspection of this line, that, so long as the chromic acid is not in defect, the two substances lose equal amounts of oxygen, according to the equation

$$2Cr_2O_3 + 3H_2O_2 = Cr_4O_3 + 3H_2O + 3O_2;$$

that when the amount of oxygen in the peroxide of hydrogen is greater than that contained in the chromic acid, more of the peroxide of hydrogen is decomposed, but never the whole amount taken, and that the amount decomposed increases with the proportion taken, until the peroxide of hydrogen contains as much as eight and a half times the amount of oxygen contained in the chromic acid; that after this point, the decomposition becomes constant, the peroxide of hydrogen losing twice the amount of oxygen lost by the chromic acid; and that no further increase in the proportion of the peroxide of hydrogen taken causes this limit to be exceeded, the final result of the change being expressed by the equation

$$2Cr_2O_3 + 6H_2O_2 = Cr_4O_3 + 6H_2O + 9O.$$

In what light are we to regard the decomposition between these extreme limits? Are we to consider that the two substances are capable of reacting in any proportion, and that the simple atomic decomposition is the limit of an indefinite action varying according to the mass? or are we not rather to believe that this apparently indefinite action is the sum of certain normal chemical changes which take place in simple atomic ratios, but which vary in absolute amount?

The following experiments indicate that the latter hypothesis is correct, and that the reaction between the extreme limits is not homogeneous, but consists of two chemical changes which are capable of being separated, from the circumstance that they take place with very unequal rapidity.

A definite period in the decomposition is marked by the disappearance of the blue compound. At this point the solution was titred, and the loss of oxygen estimated. The progress of the decomposition was followed by means of the same experiment until, finally, the maximum loss was attained. I give two series of experiments, in which the substances were taken in different proportions.

I.

Time of titration.	*r*.	*y*.	*x*.	Mean.
1. After decomposition of blue compound.	2·47	1·47	0·997 1·0033	1·001
2. After ½ an hour ..	2·446	1·446	1·277	1·277
3. After 2 hours	——	——	1·448	1·448
4. After 18 hours	——	——	1·462	1·462

II.

Time of titration.	*r*.	*y*.	*x*.	Mean.
1. Immediate.....	3·705	2·705	1·007 1·033	1·020
2. After 1 hour.....	——	——	1·593	1·593
3. After 1½ hour	——	——	1·593	1·593
4. After 2 days	——	——	1·703	1·703

It thus appears that the decomposition takes place in two stages, the former of which is complete immediately after the destruction of the blue compound, and in which the two substances lose equal amounts of oxygen; while the latter requires several hours for its completion, the solution during this time being in a continual state of change.

It is undoubtedly difficult to speak with any great probability as to the nature of the specific changes which take place, in regard to which many hypotheses may be formed.

The following view, however, is in accordance with the facts.

1. When $x = 1$, we have the formation and subsequent decomposition of the substance Cr_4O_9, according to the equations

$$2Cr_2O_3 + 3H_2O_2 = Cr_4O_9 + 3H_2O,$$
$$Cr_4O_9 = Cr_4O_3 + 3O_2.$$

2. When $x = 2$, after the reaction just expressed, the substance Cr_4O_9 is further oxidized to the oxide Cr_4O_{12}, according to the equation

$$Cr_4O_9 + 3H_2O_2 = Cr_4O_{12} + 3H_2O.$$

The body Cr_4O_{12} further decomposes with the excess of peroxide of hydrogen present, possibly with formation of the higher oxide of hydrogen, H_2O_3, and the former product, Cr_4O_9,

$$Cr_4O_{12} + 3H_2O_2 = Cr_4O_9 + 3H_2O_3.$$

That the product of the first action is in a continual state of formation and decomposition during the change, is probable from the greater permanence of the blue compound when an excess of peroxide of hydrogen is present: the presence of this body, which in a small excess of peroxide of hydrogen, has only a momentary existence, is rendered evident by the duration of the blue colour for as long as ten minutes in the presence of an excess of the peroxide. Lastly, the substance Cr_4O_9 decomposes very much more rapidly than the substance H_2O_3, *i.e*, than the other oxidized product: so that the decomposition can be broken up into its several stages in the manner described, the chemical changes which take place being represented by the system of equations,

$$\begin{aligned}
2Cr_2O_3 + 3H_2O_2 &= Cr_4O_9 + 3H_2O,\\
Cr_4O_9 + 3H_2O_2 &= Cr_4O_{12} + 3H_2O,\\
Cr_4O_{12} + 3H_2O_2 &= Cr_4O_9 + 3H_2O_3,\\
Cr_4O_9 &= Cr_4O_3 + 3O_2,\\
3H_2O_3 &= 3H_2O_2 + 3O;
\end{aligned}$$

and the result of these changes, by the equation which results from elimination between them, namely,

$$2Cr_2O_3 + 6H_2O_2 = Cr_4O_3 + 6H_2O + 9O.$$

Since the amount of oxygen is in all probability given off in successive stages, we cannot fix with certainty upon any one degree of oxidation as the blue compound.*

* I am unable to reconcile my own results with those of Barreswil, whose experiments appear to have been carefully conducted. The reaction according to this chemist is

$$\begin{aligned}
2Cr_2O_3 + H_2O_2 &= Cr_4O_7 + H_2O\\
Cr_4O_7 &= Cr_4O_3 + 2O_2,
\end{aligned}$$

the analogue of permanganic acid being formed. I have not, however, repeated the

It may be observed that, if the decomposition of permanganic acid were, as in this case, preceded by an oxidation, the corresponding degree of oxidation would be formed thus:

$$Mn_4O_7 + 5H_2O_2 = Mn_4O_{12} + 5H_2O,$$
$$Mn_4O_{12} = 2Mn_2O + 5O_2.$$

On the Oxidation effected by the Peroxide of Hydrogen.

We have seen that the peroxides of hydrogen, potassium, and barium possess certain chemical properties which do not belong to the analogous compounds of lead and manganese. An elaborate attempt* has been made to account for the different reactions of the two classes of peroxides, by the assumption that there are two kinds or varieties of oxygen, a positive and a negative variety; it is said that the peroxide of manganese acts as an agent of oxidation, because it contains the negative variety, and that the peroxide of barium acts as a reducing agent, because it contains the positive variety of this element. This hypothesis finds its only support in an imperfect and incorrect view of the facts. In truth no such fundamental distinction exists between the properties of the different peroxides as that which it is proposed thus to characterise. The chemical properties of the alkaline peroxides, as of other chemical substances, vary with the conditions in which they are placed, and the substances with which they are associated; and it is in our power so to modify these conditions as to produce with these peroxides the very same effects of oxidation as are produced by the peroxides of the other group. This is evident from the following examples, to which it would be easy to add others:—

1. An acid solution of peroxide of hydrogen causes the conversion of a solution of ferrocyanide to ferricyanide of potassium.

2. An alkaline solution of peroxide of sodium, added to a solution of a protasalt of manganese, forms hydrated peroxide of manganese.

3. An alkaline solution of peroxide of sodium oxidizes an alkaline solution of sesqui-oxide of chromium, with formation of chromate of potassium.

experiment precisely in the form in which it was made by him, and it is possible that under certain circumstances the oxidation may be arrested at this point. See Annales de Chimie, vol. xx. p. 364.

* Schönbein, Ann. Ch. Pharm., vol. cviii. p. 166.

4. A strong solution of hydrochloric acid evolves chlorine with peroxide of barium.*

That there are important differences in the reaction of the peroxide of barium and the peroxide of manganese is not to be denied. But these differences are perfectly conformable to analogy, and are similar in kind to those which distinguish other chemical substances. For experience teaches us that no two chemical substances, however close may be the analogies which connect them, have identical chemical properties. Hydrochloric acid has not all the properties of hydriodic acid; soda has not all the properties of potash; chlorine is not the same as iodine; and sodium is different from potassium. Is it then to be a matter of surprise to us that peroxide of manganese has not all the properties of peroxide of hydrogen? Is this case to have a special explanation (?). And are we to refer the different properties of these substances, not to the actual and known differences in the elements of which they consist, but to an altogether hypothetical and imaginary difference in the oxygen, which is the element common to the two bodies? In each different compound, if such conventional language be admissible, oxygen has different properties; and if we are to account for this class of differences by the assumption of different varieties of oxygen, we must assume not two forms only, but an infinite number of forms of that element. Of the precise mode in which the chemical properties of the compound are connected with the chemical properties of its constituents, we are doubtless unable to give an adequate account. But the fact of this connexion is not to be doubted. We take the oxygen of the peroxide of sodium, and transfer it to the protoxide of manganese. In this new combination it will no longer produce the effects of reduction. Again, we transfer the oxygen of the peroxide of barium to anhydrous acetic acid, and we form one of the most powerful oxidising agents with which the chemist is acquainted; while we can re-transfer this oxygen to baryta, and restore to it

* Professor Schönbein lays the greatest stress on the different behaviour of the two classes of peroxides with hydrochloric acid. He says, "Die erste Gruppe ist weiter negativ dadurch charakterisirt dass kein ihr angehöriges Superoxyd mit irgend einer wasserhaltigen Säure .... Wasserstoffsuperoxyd zu erzeugen vermag, und die zweite Gruppe dadurch, dass keines ihrer Superoxyde unter irgend welchen Umständen aus der Salzsäure oder irgend einem salzsauren Salze Chlor zu entbinden im Stande ist."—Annalen der Chemie, vol. cviii. p. 167. This sweeping statement, in regard to which the truth could have been so readily ascertained, is quite without foundation.

its original properties. It is not the oxygen which is different, but the elements differ with which the oxygen is associated.

The definite manner in which the final result is affected by modifying the conditions of the reaction, is rendered evident by the following series of experiments.

Peroxide of barium, treated with a concentrated solution of hydrochloric acid, evolves chlorine: with a dilute solution of hydrochloric acid, peroxide of hydrogen alone is formed. It was therefore probable that with hydrochloric acid of a certain degree of concentration, both reactions would simultaneously occur. This is the case, and the ratio in which the two reactions occur varies with the concentration of the hydrochloric acid, according to a definite law.

A weighed quantity of peroxide of barium was placed in a small flask, to which a delivery tube could be attached by means of a caoutchouc connector. The hydrochloric acid was poured cold upon the peroxide, the delivery tube attached, and the mixture rapidly boiled. The gas evolved was collected over a solution of iodide of potassium: it consisted of a mixture of chlorine and oxygen. The iodine formed was determined by a standard iodine solution in the usual manner. The hydrochloric acid was taken in very great excess; the same absolute amount was used in each experiment, but diluted with varying quantities of water. Since a solution of peroxide of hydrogen is decomposed on boiling into water and oxygen, we may regard the oxygen evolved as the measure of the peroxide of hydrogen formed.

Now, putting

α = the iodine contained in 1 cub. centim. of the standard iodine solution,

ϵ = the quantity of peroxide of barium employed in the experiment,

Z = the quantity of oxygen equivalent to the chlorine evolved,

$nt - t_1$ with its usual signification,

then
$$Z = \frac{O \times Ba_2O_2}{I \times 0{\cdot}2929} \times \alpha(nt - t_1).$$

In each of the experiments* 25 cub. centims. of concentrated

* The Table of these experiments is omitted.

hydrochloric acid were taken. The absolute amount of pure hydrochloric acid in this concentrated acid was experimentally determined; it amounted to 30·33 per cent. $\alpha = 0{\cdot}0029735$.

Further. Let s = the ratio of the amount of water to the amount of pure hydrochloric acid in the solution of hydrochloric acid employed; and when water is saturated with hydrochloric acid, let $s = 1$; s may be termed the ratio of saturation.

And let d = the amount of water added in each experiment to every 100 cub. centims. of the solution of hydrochloric acid employed.

Now it is estimated that, at ordinary temperatures, 100 parts of water absorb 38 parts of hydrochloric acid, while the acid employed was found to contain 30·33 per cent.

Hence s in each experiment is determined from the proportion

$$\frac{100}{38} : \frac{100 \times d}{30{\cdot}33} :: 1 : s,$$

whence

$$s = \frac{38(100 + d)}{100 \times 30{\cdot}33} = \frac{38}{30{\cdot}33} + \frac{38 \times d}{3033}$$

$$= 1{\cdot}25 + 0{\cdot}0125 \times d;$$

and if y be put $= s - 1$,

$$y = 0{\cdot}25 + 0{\cdot}0125 \times d;$$

and, lastly, if x be put = the oxygen equivalent to the chlorine evolved, $\frac{1}{2}$ the total oxygen in the peroxide of barium being assumed as 1, we have, assuming 16·02 as the total oxygen,

$$8{\cdot}01 : 1 :: Z : x,$$

whence

$$x = \frac{Z}{8{\cdot}01}.$$

We have, from the preceding experiments, the following values for d, s, y, and x:—

Experiment.	*d.*		*s.*	*y.*	*x.*
I.	0	0	1·25	0·25	1·000
II.	5	20	1·5	0·50	1·000
III.	6·25	25	1·5622	0·5622	0·9814
IV.	7·5	30	1·625	0·625	0·9567
V.	10	40	1·75	0·750	0·8263
VI.	15	60	2·00	1·00	0·5104
VII.	20	80	2·25	1·25	0·2448
VIII.	25	100	2·50	1·50	0·1167
IX.	30	120	2·75	1·75	0·0844
X.	35	140	3·00	2·00	0·0574
XI.	40	160	3·258	2·25	0·0406
XII.	50	200	3·75	2·75	0·0246
XIII.	60	240	4·25	3·25	trace.

A delineation of the results of these experiments is given in the annexed curve, Plate XXXVIII.

Catalytic Decompositions.

It has now been shown that the alkaline peroxides have a double function, and can be used as agents either of oxidation or of reduction. By certain modifications of the conditions of the experiment, we can produce separately either result. It is not unreasonable to suppose that, among the numerous and varied forms of chemical decomposition, instances would be found in which these phenomena would occur simultaneously. If this were to be the case, the result would be what is termed a contact (or catalytic) decomposition, but caused by two successive changes of a normal chemical character.

That the combination of the oxidizing with the reducing action of the peroxide of hydrogen is a cause adequate to produce the effects of catalysis, is evident from the following examples:—

I. We can successively realize the chemical changes of which the result, as regards weight, is expressed by the equations

$$MnCl + KHO = KCl + MnHO,$$
$$H_2O_2 + 2MnHO = H_2O + Mn_2H_2O_3,$$
$$H_2O_2 + Mn_2H_2O_3 + 2HCl = 3H_2O + 2MnCl + O_2.$$

The final result which ensues from the successive performance of these experiments is expressed in the following equation, derived by elimination from the preceding,

$$2KHO + 2HCl + 2H_2O_2 = 4H_2O + 2KCl + O_2.$$

which equation is again equivalent to the two equations,

$$KHO + HCl = H_2O + KCl$$

and the equation expressive of the catalytic decomposition of the peroxide of hydrogen, viz.,

$$2H_2O_2 = 2H_2O + O_2.$$

II. Again, omitting, for the sake of brevity, certain circumstances in the reactions, we can produce the results expressed by the equations

$$3H_2O_2 + Cr_4O_3 = 3H_2O + 2Cr_2O_3,$$
$$2Cr_2O_3 + 3H_2O_2 = Cr_4O_3 + 3H_2O + 3O_2,$$

whence, by elimination,

$$2H_2O_2 = 2H_2O + O_2.$$

III. Also

$$2Na_4Fe_2Cy_6 + Na_2O_2 = 2Na_2O + 2Na_3Fe_2Cy_6,$$
$$2Na_3Fe_2Cy_6 + Na_2O_2 = 2Na_4Fe_2Cy_6 + O_2,$$

whence

$$2Na_2O_2 = 2Na_2O + O_2.$$

IV. Again,

$$2HCl + H_2O_2 = 2H_2O + Cl_2,$$
$$Cl_2 + H_2O_2 = 2HCl + O_2,$$

whence

$$2H_2O_2 = 2H_2O + O_2.$$

Exp. I.—1 P. of an alkaline solution of peroxide of sodium rendered acid and titred, required 9·31 cub. centims. of permanganate solution.

A solution of protochloride of manganese was precipitated by hydrate of sodium, and 1 P. of the above solution added to it. An equivalent portion of the hydrated protoxide was converted into the hydrated peroxide of manganese.

The solution was immediately rendered acid with sulphuric acid, and 2 P. of the same solution added.

After the evolution of gas had ceased, the solution was titred. It required 9·31 cub. centims. of permanganate solution.

3 P. of peroxide had been added, and 2 P. decomposed. The

manganese was in the form of protoxide, as at the commencement of the experiment.

Exp. II.—To 1 P. of a solution of ferrocyanide of potassium, which required for its titration 5·96 cub. centims. of permanganate, was added 1 P. of an acid solution of peroxide of hydrogen, which required for titration 3·681 cub. centims. of the same solution of permanganate. An equivalent portion of ferrocyanide of potassium was formed.

The solution was rendered alkaline, and to it was added 1 P. of an alkaline solution of peroxide of sodium, which required for its titration 3·33 cub. centims. of the same permanganate solution.

The solution, rendered acid and titred, required 5·66 cub. centims. of permanganate.

Therefore a portion of peroxide equivalent to 7·15 of permanganate had disappeared.

The total peroxide added required 7·01 parts of permanganate.

In these experiments, the final is the same as the initial condition of the chemical substances, with the single exception that the peroxide of hydrogen is decomposed. If the oxidation and reduction which in the preceding examples are separately realized had taken place simultaneously and under the same general conditions, no result would have appeared but the decomposition of the alkaline peroxide, and the action would have been termed a contact action. Now, although, in the case of the catalytic decomposition of the alkaline peroxide, we are undoubtedly not able to specify in each case the precise reaction by which the final result is attained, we have yet in several instances indications that the decomposition proceeds by successive stages of this kind.

When an alkaline solution of peroxide of sodium is added to a solution of protosulphate of manganese, a precipitate is formed of hydrated peroxide of manganese. If, however, a few drops of an excessively dilute solution of protosulphate of manganese be added to an excess of peroxide of sodium, there is no precipitate, but the solution remains clear, becomes brown in colour, and the peroxide undergoes the catalytic decomposition. If a great excess of a solution of the peroxide of sodium be added to a very small quantity of freshly precipitated hydrated peroxide of manganese, the peroxide of manganese dissolves, forming the same clear brown solution. It is thus seen that the peroxide of manganese can be further oxidized by the peroxide of sodium, and that the product of this oxidation decomposes in solution the peroxide of sodium.

Again, if a solution of peroxide of sodium be added to an alkaline solution of permanganate, the latter is first reduced to manganate, the solution becoming green: on further addition of the peroxide of sodium, the solution becomes of the same clear brown colour as that produced by the oxidation of the protoxide. If, however, the peroxide be sparingly added, or if permanganate be added to this solution, a precipitate peroxide of manganese is produced. It is the compound which forms this brown solution, by the agency of which the peroxide of sodium is decomposed; and it is only when the decomposition of the latter is complete, or close upon this point, that the peroxide of manganese appears. The solution then becomes turbid, and the brown flocculent peroxide is precipitated.

It appears therefore, (1) that the protoxide of manganese can be oxidized by the peroxide of sodium to an oxide, forming a clear brown solution; (2) that permanganic acid can be reduced by the peroxide of sodium to the same substance, passing through the condition of manganate; (3) that when the reduction reaches this point, in presence of an excess of peroxide, the reduction is for a time arrested, and the catalytic decomposition commences: during this decomposition the brown compound is permanent; and when the peroxide of sodium is nearly decomposed, the reduction again proceeds, and peroxide of manganese is formed.

These phenomena may be thus accounted for. There is a point where the oxidizing action concurs with, and as it were meets, the reducing action of the peroxide of sodium; and at this point the catalysis takes place. The peroxide of manganese is formed; but so long as a sufficient excess of the alkaline peroxide is present, it is reoxidized and destroyed as fast as it is produced. By this continuous reduction and oxidation, the peroxide of sodium is gradually eliminated. Time is needed for this, as for other chemical changes; but ultimately, when but little peroxide of sodium remains, the peroxide of manganese is precipitated, being produced more rapidly than it is destroyed.

There are other examples of the same class of phenomena. When a solution of peroxide of sodium is added to a solution of a copper salt (sulphate or chloride of copper), at first there is no evolution of oxygen, but a yellowish green precipitate is formed, as was observed by Thénard; this precipitate may be thrown on a filter, and for a short time preserved. If a small portion of this precipitate be added to an alkaline solution of peroxide of sodium,

bubbles of gas are evolved, and the peroxide of sodium rapidly decomposed. If a solution of peroxide of hydrogen be mixed with a few drops of a weak solution of chloride of copper, and the whole precipitated by baryta-water, the same yellow oxide of copper is formed. The peroxide of barium is gradually decomposed; but during the decomposition this yellow oxide is permanent, and only ultimately is it decomposed into hydrated protoxide.

If a very small quantity of an ammoniacal solution of protochloride of copper be added to an alkaline solution of peroxide of sodium, the solution becomes of a yellow colour, and is gradually decomposed. During the whole time of this decomposition, which may be caused to extend over several hours, the yellow colour is permanent; but ultimately, when the whole of the peroxide is decomposed, the blue colour of the ammoniacal solution of the protoxide reappears. The yellow solution of the peroxide of copper, apart from the solution of peroxide of sodium, cannot be preserved for many minutes. The singular permanence of this compound during the decomposition is explained on the hypothesis, that it is continually reproduced as well as destroyed. In this reaction the solution of oxide of copper in potash or ammonia decomposes the alkaline peroxide into oxygen and the alkali, precisely as sulphuric acid, in the process of etherification, effects the decomposition of alcohol into ether and water. And we may regard the former event as determined by a series of alternate and inverse changes, analogous to those to which Williamson has shown the phenomena of etherification to be due, according to the equations

$$Cu_2O + Na_2O_2 = Cu_2O_2{}^* + Na_2O,$$
$$Na_2O_2 + Cu_2O_2 = Na_2O + Cu_2O + O_2.$$

It may be desirable, for the sake of clearness, to resume the points in the preceding argument. It appears, (1) that by means of the alkaline peroxides we can produce two classes of effects, oxidation and reduction, and this double function is peculiar to this group of peroxides. (2) These peroxides are decomposed by the contact of a great number of chemical substances, and this

* The oxide of copper here formed is probably the sesquioxide, which is also procured by the action of alkaline hypochlorites on the hydrated oxide of copper. The precise nature of this oxide is immaterial to the argument.

form of decomposition is also peculiar to the group. (3) The combination of an oxidizing with a reducing action is a cause adequate to produce the results of contact decomposition, and we are able, in certain cases, to imitate, as it were, the contact action by means of a successive oxidation and reduction. (4) There are instances in which we have distinct evidence that the contact decomposition is accompanied by an oxidation and subsequent reduction of the substance by which the action is determined.

In a matter so difficult to submit to the direct test of experiment, it is undoubtedly desirable to offer any view with much reservation; and it would be altogether premature to assert that this is the only form which contact decomposition can assume. Other causes may possibly lead to the same result. At the same time every new case which can be explained on these principles increases the probability of their more extended application, and raises the hope that even these obscure phenomena will ultimately be removed from the domain of conjecture and speculation, and be brought under the methods of experimental research.

XLII.—*Researches into the Chemical Constitution of Narcotine, and of its Products of Decomposition.*—Part I.

By Augustus Matthiessen, F.R.S., and G. C. Foster, B.A.

(Abridged from the Philosophical Transactions, 1863.)

Section I.—Composition of Narcotine and Cotarnine.

The existence of narcotine was indicated by Derosne as early as the year 1803, but its chemical nature remained almost entirely unknown until Robiquet,* in 1817, showed that it belonged to the class of vegetable alkaloids. Numerous analyses of narcotine were subsequently published by Dumas and Pelletier,† Pelletier,‡ Liebig,§ Regnault,‖ and others; but its composition was first determined to the general satisfaction of chemists by

* Ann. Ch. Phys. v, 275. † Ibid. xxiv, 186 and 191. ‡ Ibid. l, 271.
§ Berzelius's Jahresbericht (1832), xi, 231.
‖ Ann. Ch. Phys. lxviii, 138.

Blyth,* who, in 1844, proposed the formula $C_{46}H_{25}NO_{14}$, supporting it by numerous analyses of the double hydrochlorate of narcotine and platinum, and showing, at the same time, that it accorded well with the most trustworthy results of previous investigators, and also accounted satisfactorily for the formation of the remarkable decomposition-products of narcotine discovered by himself and by Wöhler.† Since the publication of Blyth's investigation, the formula which he proposed has been generally adopted as expressing correctly the composition of this base. More recently, however, Wertheim,‡ founding his opinion chiefly on the composition of the volatile bases obtained by distilling narcotine with potash, has maintained the existence of two additional varieties of narcotine, homologous with that examined by Blyth, and represented respectively by the formulæ $C_{44}H_{23}NO_{14}$ and $C_{48}H_{27}NO_{14}$; while Hinterberger§ has analysed a compound of chloride of mercury with what he considers as a fourth variety, still homologous with the preceding, and represented by the formula $C_{42}H_{21}NO_{14}$.

Such being the results of previous investigations, it was plainly necessary to begin any new research into the chemical nature of narcotine by endeavouring to ascertain, by direct analysis, whether there existed in reality more than one kind of narcotine, and, if so, which of these kinds was being operated upon.

Analysis of six samples of narcotine prepared from different kinds of opium gave results agreeing with the formula $C_{44}H_{23}NO_{14}$ much better than with $C_{46}H_{25}NO_{14}$, as the following comparison will show:—

	Calculated. $C_{44}H_{23}NO_{14}$.	Mean of Analyses.	Calculated. $C_{46}H_{25}NO_{14}$.
Carbon..	63·92	63·78	64·63
Hydrogen	5·57	5·76	5·85
Nitrogen	3·39	3·32	3·28
Oxygen..	27·12	27·14	26·24
	100·00	100·00	100·00

We are therefore led to adopt the formula $C_{44}H_{23}NO_{14}$, or preferably ~~$C_{22}H_{23}NO_7$~~, as that which most correctly expresses the composition of the substance analysed. Moreover, since all the

* Chem. Soc. Mem. ii, 167.
† Ann. Ch. Pharm. l, 1.
‡ J. pr. Chem. liii, 431.
§ Ann. Ch. Pharm. lxxxii, 312.

different samples of narcotine which we were able to procure gave on analysis nearly identical results, the difference between the highest quantity of carbon and the lowest amounting in ten analyses to only 0·63 per cent., we conclude that there is no sufficient evidence of the existence of more than one kind of narcotine, especially as we believe that the observations which formerly gave rise to the contrary opinion are explained by an experiment to be hereinafter described.

If the formula $C_{22}H_{23}NO_7$ be adopted for narcotine, it is impossible to account in any simple manner for the well-known decomposition of that substance, under the influence of oxidising agents, into opianic acid and cotarnine, unless the received formula of either one or other of these bodies be also modified.

It seemed impossible to doubt the accuracy of the formula $C_{10}H_{10}O_5$ for opianic acid, but nevertheless, for the sake of greater certainty, we have repeated the analysis of this acid, though with no other result than a fresh confirmation of the admitted formula.

On the other hand, our analyses of cotarnine lead us to adopt the formula $C_{12}H_{13}NO_3$, in preference to the usual formula, $C_{13}H_{13}NO_3$, which represents that substance as containing one atom of carbon more. The following analyses were made with crystallised cotarnine prepared by the action of dilute nitric acid on narcotine, the method recommended by Anderson for the preparation of pure cotarnine: it had a slight yellow or buff colour, which it was found impossible to remove.

	Calculated.		Mean of Analyses.	Calculated. $C_{13}H_{15}NO_4$.
C_{12}	144	60·76	60·69	62·65
H_{15}	15	6·33	6·52	6·02
N	14	5·90	5·87	5·62
O_4	64	27·01	26·92	25·71
$C_{12}H_{13}NO_3,HO_2$..	237	100·00	100·00	100·00

These results were confirmed by analyses of the chloroplatinate of cotarnine.

The adoption of the formula $C_{12}H_{13}NO_3$* for cotarnine enables

* The formula originally proposed for cotarnine by Wöhler, but which he himself only regarded as provisional, was $C_{26}H_{13}NO_5$; Blyth's formula was $C_{25}H_{13}NO_6$; the formula $C_{13}H_{13}NO_3$ was proposed by Gerhardt (Précis de Chimie Organique, 1845, vol. ii. p. 298).

us to represent its formation by the action of oxidising agents on narcotine, by means of a very simple equation,—

$$\underset{\text{Narcotine.}}{C_{22}H_{23}NO_7} + O = \underset{\text{Cotarnine.}}{C_{12}H_{13}NO_3} + \underset{\text{Opianic acid.}}{C_{10}H_{10}O_5},$$

and, as will be shown hereafter, it is further supported by the manner in which cotarnine is decomposed by nitric and hydrochloric acids.

Assuming the accuracy of the formulæ here proposed as sufficiently established, we next endeavoured to ascertain the chemical constitution of narcotine, by studying the action of various reagents on cotarnine and on its other principal derivative, opianic acid. Hitherto we have made but few experiments on the action of reagents on narcotine itself, from the conviction that their results would hardly be intelligible without a previous knowledge of the transformations of the bodies into which it splits up with so much ease.

It appears, as the result of a good many trials, that the following is perhaps the most advantageous method of transforming narcotine into opianic acid and cotarnine. 100 grms. of narcotine is dissolved in a considerable excess of dilute sulphuric acid (150 grms. acid and 1500 grms. water), the solution is heated to boiling, and 150 grms. finely powdered peroxide of manganese* is then added as quickly as possible, care being taken that it does not cause the liquid to froth over; when the whole quantity of peroxide of manganese has been added, the mixture is quickly filtered through a funnel surrounded by boiling water. The filtrate, on cooling, becomes half-solid, from the separation of crystals of opianic acid, and by twice recrystallising this product from boiling water, it is obtained sufficiently pure for most purposes, though still retaining a slight brownish-yellow colour, which can be got rid of, when needful, by boiling the acid with a dilute solution of hypochlorite of sodium, in the manner indicated by Wöhler.

The cotarnine contained as sulphate, together with a large quantity of sulphate of manganese, in the original mother-liquor of the opianic acid, may be conveniently extracted therefrom as follows. The mother-liquor is mixed with a quantity of milk of lime sufficient to neutralise the free sulphuric acid and to precipitate part of the manganese, then, without filtering, an excess of

* 100 parts of our oxide of manganese corresponded to 60 parts of pure peroxide.

carbonate of sodium is added and the whole is heated to boiling for a few minutes, in order to precipitate completely the manganese and lime (or the neutralisation and precipitation may be effected entirely by means of carbonate of sodium, without using lime). The mixture is then filtered, first through calico and afterwards, if needful, through paper; the filtrate is neutralised with dilute sulphuric acid, evaporated rapidly to a small bulk, allowed to cool completely, poured off from any sulphate of sodium that may have crystallised out, and finally mixed with an excess of strong potash- or soda-ley, whereby the cotarnine is precipitated.

It is a matter of some importance for the successful preparation of cotarnine in this manner, that its extraction from the original mother-liquors containing it should be proceeded with without much delay, otherwise the quantity obtained is small, and its colour dark. Under all circumstances, the odour of ammonia, or methylamine, is perceptible on adding potash for the final precipitation of the cotarnine, and this odour is strongest when a long time has elapsed during the previous parts of the process. The decomposition which is thus indicated, appears to lessen the amount of product obtained in two ways: not only is the quantity of cotarnine existing in the solution diminished by the amount that has suffered decomposition, but the resulting volatile alkali seems to prevent the precipitation of the unaltered base.

Cotarnine that is very dark-coloured may be decolorised, to a considerable extent, by dissolving it in hydrochloric acid, digesting the solution upon bone-charcoal, and re-precipitating with potash; but we have never, by any process, succeeded in obtaining cotarnine quite without colour.

Section II.—Decompositions and Derivatives of Opianic Acid.

1. *Action of Hydrochloric Acid.*—When opianic acid is heated with three or four times its weight of ordinary strong hydrochloric acid, either to 100° C. in a sealed tube, or to the boiling-point of the acid in an open vessel, it is decomposed, with evolution of chloride of methyl and carbonic acid; and on evaporating the remaining solution, first on the water-bath, then at the common temperature over lime and sulphuric acid, a residue is obtained which appears to consist of three distinct crystallisable substances; but the ease with which at least one of them undergoes alteration

by heat or exposure to air, and the difficulty of completely separating them from each other, have hitherto prevented us from making a thorough examination of these products, and we therefore postpone to a future communication, any further description of them.*

Opianic acid seems to undergo a similar decomposition when boiled with fuming *hydriodic acid;* in this case iodide of methyl is given off, without separation of iodine, but we have not found it possible to remove the excess of hydriodic acid from the residue without destroying the organic constitutents.

2. *Action of Potash.*—When opianic acid is mixed with a large excess of potash-ley, and the liquid is evaporated nearly to dryness, the acid splits up into meconin and hemipinic acid. No blackening occurs unless too small a quantity of potash is employed; but when a certain degree of concentration is reached, the decomposition appears to take place almost instantaneously: the mixture, which up to that point is a thick fluid, suddenly becomes nearly solid, and as soon as this change has occurred, no more opianic acid can be detected in the mass. The decomposition may even be effected, without the application of external heat, by simply mixing opianic acid with a very strong and warm solution of potash.

In an experiment made in order to ascertain the proportions in which meconin and hemipinic acid are formed in this reaction, 42 grms. of opianic acid yielded—

13·5 grms. pure meconin,
18·5 grms. pure hemipinic acid (weighed as hemipinate of ammonium),
4·7 grms. meconin and hemipinic acid mixed,
5·0 grms. uncrystallisable residue.

Total .. 41·7 grms.

* According to Wöhler, opianate of ethyl is not formed when a solution of opianic acid in alcohol is saturated with hydrochloric acid. The experiments described in the text made it seem probable that the non-formation of opianic ether under these circumstances might be owing to the decomposition of the opianic acid; but, on sealing up opianic acid with an alcoholic solution of hydrochloric acid and heating it in the water-bath for an hour, it was found that opianate of ethyl was formed in abundance. The ether was precipitated by pouring the contents of the tube into water, and purified by crystallisation from alcohol. Thus obtained, it formed hemispherical masses of brilliantly white radiating needles, insoluble in water or dilute alkalis, melting to a colourless oil under hot water, and easily soluble in alcohol and ether. In the dry state it melts at 88° C.

In another experiment, a small quantity of the mixture of opianic acid and potash was boiled down in a small flask, fitted with a glass tube about a yard long, bent vertically downwards just outside the cork, and dipping by its lower end into mercury. When the reaction had taken place, the flask was allowed to cool, and the mercury then rose in the vertical tube to within about an inch of the height of the barometer at the time; thus proving that no permanent gas had been evolved. Hence the following equation —according to which, 42 grammes opianic acid should yield 19·4 grammes meconin and 22·6 grammes hemipinic acid—may be taken to represent the decomposition :—

$$\underset{\text{Opianic acid.}}{2C_{10}H_{10}O_5} = \underset{\text{Meconin.}}{C_{10}H_{10}O_4} + \underset{\text{Hemipinic acid.}}{C_{10}H_{10}O_6}.$$

The following process was adopted for the purification of the meconin and hemipinic acid thus formed. The alkaline mass obtained by heating opianic acid with potash, was dissolved in a moderate quantity of warm water, and mixed with an excess of hydrochloric acid: in this way the meconin was caused to separate out as an oil, and to carry down most of the hemipinic acid. After the acidified liquid has been allowed to cool completely, it was poured off from the solid cake of meconin and hemipinic acid which had formed at the bottom, and evaporated to a small bulk, so as to cause the separation of the greater part of the chloride of potassium; this was washed with alcohol; the alcoholic washings were mixed with the concentrated mother-liquor, and the fresh quantity of chloride of potassium, which was thus precipitated, was removed by filtration or decantation, and the clear liquid was evaporated on the water-bath nearly to dryness; the residue thus obtained was again treated with alcohol, in order to separate the last portions of chloride of potassium, and the alcoholic solution filtered and evaporated. The product of these operations, together with the original precipitate of meconin and hemipinic acid, was next dissolved in boiling water, and the solution made slightly alkaline with ammonia. Nearly the whole of the meconin then crystallised out as the solution cooled, and was obtained quite pure by recrystallisation from water; the hemipinic acid, on the other hand, remained in solution as hemipinate of ammonium, together with a small quantity of meconin; for although this substance dissolves only very slightly in cold water,

it is perceptibly more soluble in a solution of hemipinate of ammonium. In order, therefore, to complete the purification of the hemipinic acid, the solution of its ammonium-salt was precipitated with acetate of lead, and the hemipinate of lead, after being thoroughly washed, was decomposed under water by hydrosulphuric acid.

Meconin and hemipinic acid thus prepared were found to have all the properties ascribed to them by previous observers. Their identity was further established by analysis.

Analyses of Meconin.

	Calculated.		Found.	
			I.	II.
C_{10}	120	61·85	61·34	61·39
H_{10}	10	5·15	5·32	5·28
O_4	64	33·00	——	——
$C_{10}H_{10}O_4$ ..	194	100·00		

Chloromeconin was prepared from this product by treating it in aqueous solution with hypochlorite of sodium and hydrochloric acid.

	Calculated.	Found.	
	$C_{10}H_9ClO_4$.	I.	II.
Chlorine per cent.	15·54	15·46	15·76

Nitromeconin was also prepared, but not analysed.

Analyses of Hemipinic Acid.

	Calculated.		Found.	
			I.	II.
C_{10}	120	53·10	53·01	53·09
H_{10}	10	4·42	4·68	4·62
O_6	96	42·48	——	——
$C_{10}H_{10}O_6$ ..	226	100·00		

3. *Action of Nascent Hydrogen.*—When an aqueous solution of opianic acid is warmed for several hours with sodium-amalgam, the subsequent addition of hydrochloric acid causes a precipitate of meconin. The formation of meconin is not due, in this case, to

the decomposition of the opianic acid by the soda formed from the sodium-amalgam; for it takes place in a dilute solution, and at a temperature very much below that at which opianic acid is decomposed under the influence of alkali; the quantity of meconin formed from a given weight of acid is also considerably greater than that produced under the latter circumstances; for instance, 5 grms. opianic acid gave 3·65 grms. pure meconin, whereas 5 grms. opianic acid decomposed by alkali would yield 2·3 grms. meconin and 2·7 grms. hemipinic acid. The barely possible supposition that the additional quantity of meconin is owing to the reduction of hemipinic acid formed in a previous stage of the reaction, is excluded by the fact that hemipinic acid is not acted on by sodium-amalgam in presence of water. Moreover, opianic acid is similarly converted into meconin by the action of zinc and dilute sulphuric acid. Hence, the transformation consists in a direct reduction or deoxidation of the acid under the influence of nascent hydrogen:

$$\underset{\text{Opianic acid.}}{C_{10}H_{10}O_5} + H_2 = \underset{\text{Meconin.}}{C_{10}H_{10}O_4} + H_2O.$$

According to this equation, 5 parts of opianic acid correspond to 4·6 parts of meconin.

Chemists have long been aware of the simple relation subsisting between the formulæ of

Meconin	$C_{10}H_{10}O_4$,
Opianic acid	$C_{10}H_{10}O_5$,

and

Hemipinic acid.....	$C_{10}H_{10}O_6$;

the foregoing experiments prove that this relation is not confined to the formulæ, but that the bodies themselves are intimately connected. Hence it is evident that, in order to arrive at a knowledge of the constitution of opianic acid, the chemical nature of the other two members of the group must also be examined. The experiments which we have made in this direction are still very far from complete; they relate principally to the action of acids on meconin and hemipinic acid, and the following are the most important results yet obtained.

Action of Hydriodic and Hydrochloric Acids on Meconin.—When meconin is boiled with concentrated hydriodic acid, a con-

siderable quantity of iodide of methyl is formed, but the other products of the reaction are so unstable that it has not been found possible to remove the excess of hydriodic acid without completely destroying them. It was not till after many attempts to purify the products thus formed, that it was found that meconin undergoes a similar decomposition when heated in a sealed tube, to a little above 100°, with three times its weight of strong hydrochloric acid. The chloride of methyl, formed under these circumstances, quickly volatilises when the tube is opened, and by careful evaporation, over lime and sulphuric acid, a crystalline residue may be obtained, whence it is possible to remove completely the excess of hydrochloric acid; but it has not yet been further investigated.

Action of Hydriodic Acid on Hemipinic Acid.—Hemipinic acid is decomposed, when boiled with concentrated hydriodic acid, into carbonic acid, iodide of methyl (boiling point 42°·8 C., vapour-density 5·05: calculated vapour-density 4·92), and an acid of the formula $C_7H_6O_4$. It will be seen that the composition of this acid is intermediate between that of salicylic acid, $C_7H_6O_3$, and that of gallic acid, $C_7H_6O_5$, and, as will be seen by the description which follows, it is analogous to these acids in some of its properties. Accordingly, in order to recall the fact of its containing one atom of oxygen less than gallic acid, we propose to name it provisionally *hypogallic acid*, reserving to ourselves to suggest if possible a more appropriate name when its chemical relations shall have been more thoroughly investigated. The reaction, by which these products are formed, takes place according to the equation—

$$\underset{\text{Hemipinic acid.}}{C_{10}H_{10}O_6} + 2HI = CO_2 + \underset{\text{Iodide of methyl.}}{2CH_3I} + \underset{\text{Hypogallic acid.}}{C_7H_6O_4}.$$

Hypogallic acid, when pure, is only slightly soluble in cold water, but dissolves easily in hot water, alcohol, and ether; its solution reacts strongly acid with litmus-paper. It separates from hot water in small prismatic crystals, united into stellate groups, and containing $1\frac{1}{2}$ atom water of crystallisation, which they lose at 100°. The acid melts at about 180°, but as it begins to decompose even at a lower temperature, its melting-point could not be accurately ascertained. Dried at 100° C., it gave the following results on analysis:—

	Calculated.		Found.		
			I.	II.	III.
C_7	84	54·55	54·34	54·46	54·35
H_6	6	3·89	3·97	3·95	3·82
O_4	64	41·56	——	——	——
$C_7H_6O_4$	154	100·00			

	Calculated.		Found.		
			I.	II.	III.
$C_7H_6O_4$	154	85·08	——	——	——
$H_3O_{1½}$	27	14·92	14·80	14·63	15·08
$C_7H_6O_4,1½H_2O$..	181	100·00			

Hypogallic acid gradually turns brown when heated in the air to a little above 100° C.; the same change occurs more quickly when a solution of it, especially if neutral or alkaline, is evaporated. Added to solution of *nitrate* or *ammonio-nitrate of silver*, it causes an immediate precipitation of metallic silver, even in the cold; with *sulphate of copper* and a slight excess of potash it gives a yellowish green solution from which an orange-yellow precipitate is thrown down on warming; in a mixture of *sesquichloride of iron and red prussiate of potash*, it immediately produces a blue precipitate; when boiled with solution of *corrosive sublimate*, it reduces it to calomel. With *sesquichloride of iron*, it gives an intense indigo-blue coloration, which is changed to violet by a very small quantity of ammonia, and to blood-red by excess of ammonia, no precipitate being produced, unless too much chloride of iron has been used; the colour is destroyed by strong acids, but restored by neutralisation with alkali, and partially by addition of water. A solution of the acid immediately becomes brown on addition of *alkali*, the colour quickly becoming darker by exposure to the air. With *ammonia and chloride of barium* or *calcium*, it gives a brownish white flocculent precipitate; with *acetate of lead*, a pale yellow precipitate.

Hypogallic acid is decomposed by heat into carbonic acid and a substance which solidifies in the neck of the retort to a colourless crystalline mass. The decomposition begins at about 170° C., and goes on rapidly at 200°. The crystalline product melts, in the crude state, at about 90° C.; it dissolves easily in water and crystallises in needles when the solution is evaporated. It is rapidly

attacked by nitric acid, even when diluted, giving a red-brown solution. With sesquichloride of iron it gives a bluish-black amorphous precipitate; with acetate of lead it gives a white or yellowish-white precipitate, soluble in an excess of acetic acid. It slowly assumes a darker colour by exposure to air in contact with alkali. This substance has not yet been prepared in sufficient quantity for complete investigation.

In addition to hypogallic acid, no less than three other acids are known, having the same composition, and resembling it to a remarkable degree in some of their most characteristic properties. They are carbohydrochinonic acid* (obtained by Otto Hesse by the action of bromine in presence of water on chinic acid), protocatechuic acid† (obtained by Strecker as a product of the action of fused potash on piperic acid), and oxysalicylic acid‡ (obtained by Lautemann by decomposing iodosalicylic acid with potash). All these acids are described as having about the same solubility in water, alcohol, and ether, as hypogallic acid; like it, they all give a dark coloration with the smallest trace of sesquichloride of iron; they all reduce nitrate of silver; they all become dark brown when mixed with alkali and exposed to the air; all give a yellowish-white precipitate with acetate of lead; and at a high temperature they are all decomposed into carbonic acid and oxyphenic acid or hydrochinone.§ Nevertheless, no two of these acids appear to have quite the same properties. The following are the most important points in which differences have been observed. Hypogallic acid crystallises with $1\frac{1}{2}$ molecule of water (14·9 per cent.), carbohydrochinonic and protocatechuic acids with 1 molecule (10·4 per cent.), and oxysalicylic acid without water. Hypogallic and oxysalicylic acids give a dark blue colour with sesquichloride of iron, the other two acids a dark green colour. Hypogallic acid reduces nitrate of silver immediately in the cold; carbohydrochinonic acid reduces it slowly in the cold, rapidly when boiled; oxysalicylic acid has no action on nitrate of silver in the cold, but reduces it completely when boiled. Carbohydrochinonic acid reduces cuprous oxide from a mixture of cupric acetate, tartaric acid,

* Ann. Ch. Pharm. cxii, 52 (1859); cxiv, 292; cxxii, 221.

† Ibid. cxviii, 280.

‡ Ibid. cxviii, 372; more fully cxx, 311.

§ The product obtained by the action of heat on hypogallic acid does not fully agree in its reactions with either of these bodies, so far as yet examined.

and excess of potash; protocatechuic acid causes no reduction of the same solution. Hypogallic acid causes a precipitate in a mixture of chloride of barium and ammonia; protocatechuic acid only on addition of alcohol.

Whether some of these differences may not be due to accidental causes, depending on the different sources and modes of preparation of the several acids, is a question that readily suggests itself, but it can be answered only by further investigation.

Action of Hydrochloric acid on Hemipinic Acid.—Hemipinic acid is rapidly decomposed when heated with two or three times its weight of strong hydrochloric acid, either in a sealed tube to about 110° or in an open vessel connected with a condenser, so arranged that the condensed vapour flows back into the mixture, and with an apparatus for evolving gaseous hydrochloric acid, whereby the liquid can be kept constantly saturated with that acid. The products of the reaction are chloride of methyl, carbonic acid, and an acid crystallising in beautiful long transparent prisms.

This acid is almost insoluble in cold water, and not much more soluble in boiling water; alcohol and ether dissolve it more easily. When heated it begins to sublime, without decomposition, at about 200° C., and supports a temperature of more than 245° without any further change, though at a still higher temperature it melts, and solidifies again on cooling to a crystalline mass. It dissolves in strong sulphuric acid, and is precipitated unchanged on addition of water. It gives no coloration with sesquichloride of iron; with nitrate of silver it gives a white precipitate, which blackens on boiling. It gave, on analysis, numbers agreeing nearly with the formula $C_8H_8O_4$.*

	Calculated.		Found.
C_8	96	57·14	56·64
H_8	8	4·76	5·17
O_4	64	38·10	——
$C_8H_8O_4$ ..	168	100·00	

The formation of this body therefore probably takes place in accordance with the equation—

* *Postscript*, Oct. 5th, 1863.—Since this paper was written, this acid has been again prepared, and the above formula confirmed by additional analyses, as well as by the preparation and analysis of a dinitro-derivative = $C_8H_6(NO_2)_2O_4,H_2O$.

$$\underset{\text{Hemipinic acid.}}{C_{10}H_{10}O_6} + HCl = CO_2 + CH_3Cl + C_8H_8O_4.$$

We hope to give a more complete description of it in a future communication.

By the prolonged action of hydrochloric acid on the mother-liquor from which this acid has crystallised, hypogallic acid appears to be formed. The product thus obtained has not yet been analysed, but it is identical in all its qualitative reactions with that formed by the action of hydriodic acid on hemipinic acid.

Nascent Hydrogen, resulting from the action of sodium-amalgam on an aqueous solution of hemipinic acid, leaves that acid unacted upon, as already stated. A portion of hemipinic acid that had been subjected for a long time to the action of sodium-amalgam was converted into silver-salt, the salt being precipitated in two fractions. Both portions were found on analysis, to consist of pure hemipinate of silver, and no other organic substance than hemipinic acid could be detected in the solution.

We may here mention a peculiar property of hemipinate of barium which does not seem to have been before observed, but which has often been of service to us as affording the means of recognising hemipinic acid when present only in small quantity.

When a solution of hemipinic acid is neutralised with baryta-water, or when solutions of hemipinate of ammonium and chloride of barium are mixed together, the liquid remains clear for a long while if left to itself; but if it is boiled for a short time, small, shining, crystalline plates of hemipinate of barium are precipitated and soon fill the whole liquid, if the solutions used were not too dilute. On allowing the liquid to cool, it redissolves this precipitate, and becomes almost or quite clear; but after standing for a few hours, or for a day or two, according as more or less of the salt is contained in it, it again deposits hemipinate of barium, but this time in the form of feathery tufts of very small silky needles; if the liquid be now again heated, these feathery crystals dissolve, and the crystalline plates already mentioned make their appearance once more.

Section III.—Decompositions and Derivatives of Cotarnine.

1. *Action of Nitric Acid.*—By gently heating cotarnine with dilute nitric acid, we have obtained nitrate of methylamine and a new acid, *cotarnic acid,* but have not hitherto found out the conditions necessary for the certain production of the latter substance, many attempts to obtain it having been completely unsuccessful.

Cotarnic acid dissolves easily in water, giving a solution which reacts strongly acid with litmus-paper: it dissolves to a less extent in alcohol, and is precipitated from its alcoholic solution by ether. It yields no trace of cyanide when heated with metallic sodium in excess, and is thus proved to contain no nitrogen. It gives a white precipitate with acetate of lead, and is not affected by sesquichloride of iron. Nitrate of silver throws down a very stable silver-salt, which may be crystallised from boiling water, in which it is slightly soluble, without alteration. This salt contains $C_{11}H_{10}Ag_2O_5$.

	Calculated.		Found.	
			I.	II.
C_{11}	132	30·14	29·22	30·10
H_{10}	10	2·27	2·16	2·17
Ag_2	216	49·32	49·14	49·35
O_5	80	18·27	——	——
$C_{11}H_{10}Ag_2O_5$ ..	438	100·00		

Hence cotarnic acid must contain $C_{11}H_{12}O_5$, and its formation from cotarnine must take place according to the equation

$$\underset{\text{Cotarnine.}}{C_{12}H_{13}NO_3} + 2H_2O = \underset{\text{Cotarnic acid.}}{C_{11}H_{12}O_5} + \underset{\text{Methylamine.}}{CH_5N}.$$

The formation of methylamine in this reaction was proved by the analysis of its chloroplatinate.

Cotarnine heated with undiluted nitric acid was found to yield oxalic and apophyllic acids, in accordance with the statements of Wöhler and Anderson.

2. *Action of Hydrochloric Acid.*—Cotarnine heated with three times its weight of strong hydrochloric acid to about 140° C., in a sealed tube, is decomposed into chloride of methyl—identified, *inter alia,* by its formation of the solid hydrate described by

Bäyer *—and a substance which crystallises in very small, pale yellow, silky needles. This body we designate, provisionally, *hydrochlorate of cotarnamic acid*, assigning to it the formula $C_{11}H_{13}NO_4,HCl$, which, though not agreeing perfectly with the analyses hitherto obtained, expresses their results more closely than any other formula that seems equally probable. The substance was purified for analysis by several crystallisations from water slightly acidulated with hydrochloric acid, and was dried *in vacuo* over lime and sulphuric acid.

	Calculated.		Mean of analyses.
C_{11}	132	50·87	49·94
H_{14}	14	5·40	5·70
N.....	14	5·40	5·73
O_4	64	24·65	24·61
Cl	35·5	13·68	14·02
$C_{11}H_{13}NO_4.HCl$	259·5	100 00	100·00

Assuming for the present the accuracy of the proposed formula, the action of hydrochloric acid on cotarnine will be represented by the following equation:—

$$\underset{\text{Cotarnine.}}{C_{12}H_{13}NO_3} + H_2O + 2HCl = CH_3Cl + \underset{\text{Hydrochlorate of cotarnamic acid.}}{C_{11}H_{13}NO_4,HCl}.$$

Hydrochlorate of cotarnamic acid is only slightly soluble in cold water, but is very soluble in hot water; it is less soluble in alcohol than in water, and almost insoluble in ether. When dissolved in hot water, it always undergoes partial decomposition, as is indicated by the separation of an orange-coloured granular precipitate if the quantity of water used is only moderate; when more water is employed, this precipitate remains dissolved, the smallest trace imparting a bright orange colour to the solution. A similar precipitate (cotarnamic acid, $C_{11}H_{13}NO_4$?) is thrown down on cautiously adding an alkali, or alkaline carbonate or sulphite, to an aqueous or slightly acid solution of hydrochlorate of cotarnamic acid; this precipitate regenerates the original compound when treated with hydrochloric acid; it dissolves with

* Ann. Ch. Pharm. ciii, 183.

orange colour in excess of alkali, giving a solution which rapidly becomes brown in the air; by washing with water, out of contact with air, it may be obtained quite free from chlorine. The hydrochlorate dissolves without alteration in water containing a small quantity of free hydrochloric acid; the solution, which is but slightly coloured at first, gradually acquires a beautiful dark-green colour by exposure to the air. If nitric acid is slowly added to a solution of the compound in boiling water, the portions of the liquid with which the acid comes in contact, assume a fine opaque crimson colour when seen by reflected light, but appear of a transparent orange tint when seen by transmitted light. After a few minutes, a slight effervescence takes place, and this effect disappears. Hydrochlorate of cotarnamic acid mixed with a slight excess of dilute sulphuric acid, and evaporated nearly to dryness on a water-bath, acquires a fine crimson colour, rivalling that of acetate of rosaniline; this colour is destroyed by addition of water, but it appears again when the water is evaporated. Nitrate of silver added in excess to a hot solution of the hydrochlorate is rapidly reduced.

Hydriodic and *sulphuric acids* appear to act upon cotarnine in the same way as hydrochloric acid. With hydriodic acid, iodide of methyl is formed in unmistakable quantity; the formation of a methyl-compound by the action of sulphuric acid was not proved, but in both cases appropriate treatment of the resulting solutions yielded hydrochlorate of cotarnamic acid, with all its characteristic properties above described.

We have not yet obtained cotarnamic acid itself, nor any of its compounds except the hydrochlorate, in a state that invited analysis; but we hope to be able to do so on continuing our experiments, and thus to remove any uncertainty that may at present exist as to the true formula of this substance.

3. *Action of Potash.*—Cotarnine distilled with caustic potash yields ammonia and methylamine, but apparently no di- or trimethylamine, or other similar compounds.

Section IV.—Conclusion.*

The foregoing results, although far from complete in respect to many points, are sufficient to indicate, at least partially, the che-

* The substance of what follows here was communicated to the Chemical Section of the British Association, at its late meeting in Newcastle-upon-Tyne.

mical nature of the substances to which they relate, and we accordingly venture to point out the most important conclusions which, in our opinion, may be drawn from them, and the relation in which the substances and transformations that have been described appear to stand to those wherewith our acquaintance is more complete.

1. The analytical results given at the beginning of this paper appear to prove that the composition of narcotine is *always* represented by the formula $C_{22}H_{23}NO_7$. An explanation of the results which led Wertheim to admit the existence of other varieties of the base, is, perhaps, furnished by the following experiment: 20 grammes of narcotine, boiled with an excess of concentrated hydriodic acid, yielded 19 grammes of pure iodide of methyl, a quantity which is nearly in the proportion of 3 molecules of iodide of methyl to 1 molecule of narcotine ($C_{22}H_{23}NO_7 : 3CH_3I = 413 : 436 = 20 : 21{\cdot}1$). It is thus proved that narcotine is so constituted as to allow of the easy separation of three atoms of methyl; and hence it is conceivable that, in Wertheim's experiments of distilling narcotine with caustic potash, there may have been formed, according to the circumstances under which he operated, methylamine, dimethylamine, or trimethylamine, and that, the volatile base which he regarded as propylamine (C_3H_9N) and the formation of which induced him to admit the existence of "propyl-narcotine" ($= C_{24}H_{27}NO_7$), was in reality its isomer trimethylamine.

This result, according to which narcotine must be regarded as a trimethylised compound, may, at first sight, seem to render probable the existence of other varieties of the base, wherein the whole or part of the methyl is replaced by ethyl, or by other similar radicles. Such an inference, however, would hardly be justified by analogy, for numerous substances are known to occur in nature, containing, in some form or other, methyl as one of their constituents, whereas the corresponding ethylised compounds are either entirely unknown, or have been obtained only as artificial products. We may mention as examples, methyl-salicylic acid, or oil of Wintergreen, methyl-conine (v. Planta and Kekulé), brucine (Strecker), codeine (Anderson) caffeine (Wurtz, Rochleder, Strecker), and several others of the natural alkaloids.

2. The transformation of opianic acid into meconin and hemipinic acid, when heated with potash, if viewed as a direct trans-

ference of oxygen from one molecule of opianic acid to another ($C_{10}H_{10}O_5 - O$ = meconin; $C_{10}H_{10}O_5 + O$ = hemipinic acid), is without any exact counterpart, so far as we are aware, among other known transformations. The conversion of opianic acid into meconin by nascent hydrogen is also, if regarded as a process of direct deoxidation, an example of a kind of reaction which, among organic bodies, is scarcely less exceptional. We are, therefore, inclined to believe that the first product in both these cases is not meconin, but a hitherto unknown hydrate of meconin, $C_{10}H_{12}O_5$, from which meconin is produced by the subsequent loss of the elements of water. If this be admitted, the two reactions appear perfectly analogous to many of those with which chemists are most thoroughly acquainted. We should then have (substituting for potash, in the first reaction, its equivalent of water)—

$$\underset{\text{Opianic acid.}}{2C_{10}H_{10}O_5} + H_2O = \underset{\substack{\text{Hypothetical}\\ \text{Hydrate of meconin.}}}{C_{10}H_{12}O_5} + \underset{\text{Hemipinic acid.}}{C_{10}H_{10}O_6},$$

strictly analogous to

$$\underset{\text{Oil of bitter almonds.}}{2C_7H_6O} + H_2O = \underset{\text{Benzylic alcohol.}}{C_7H_8O} + \underset{\substack{\text{Benzoic acid.}\\ \text{(Cannizzaro.)}}}{C_7H_6O_2};$$

and

$$\underset{\text{Opianic acid.}}{C_{10}H_{10}O_5} + H_2 = \underset{\substack{\text{Hypothetical}\\ \text{Hydrate of meconin.}}}{C_{10}H_{12}O_5},$$

strictly analogous to

$$\underset{\text{Oil of bitter almonds.}}{C_7H_6O} + H_2 = \underset{\substack{\text{Benzylic alcohol.}\\ \text{(Friedel.)}}}{C_7H_8O},$$

and to

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} + H_2 = \underset{\substack{\text{Mannite.}\\ \text{(Linnemann.)}}}{C_6H_{14}O_6}.$$

Considered in this light, the two transformations in question may be regarded as giving additional weight to the views of Berthelot, who pointed out some years ago that, in several particulars, opianic acid exhibits the characters of an aldehyde rather than of a well marked acid. Opianic acid and its congeners thus appear to form a series, comparable to many that are known in organic chemistry: for instance—

Meconin	$\overline{C}_{10}H_{10}\overline{O}_4$,
Hypothetical hydrate of meconin	$\overline{C}_{10}H_{12}\overline{O}_5$,
Opianic acid	$\overline{C}_{10}H_{10}\overline{O}_5$,
Hemipinic acid	$\overline{C}_{10}H_{10}\overline{O}_6$.
Benzylene	$\overline{C}_7H_6$,
Benzylic alcohol	$\overline{C}_7H_8\overline{O}$,
Oil of bitter almonds	$\overline{C}_7H_6\overline{O}$,
Benzoic acid	$\overline{C}_7H_6\overline{O}_2$.
Mannitan	$\overline{C}_6H_{12}\overline{O}_5$,
Mannite	$\overline{C}_6H_{14}\overline{O}_6$,
Glucose	$\overline{C}_6H_{12}\overline{O}_6$,
Mannitic acid	$\overline{C}_6H_{12}\overline{O}_7$.

3. The action of hydrochloric and hydriodic acids upon opianic acid, meconin, and hemipinic acid, shows that each of these compounds contains methyl. The reaction which gives rise to hypogallic acid, shows that each molecule of hemipinic acid contains two atoms of methyl, and there is every reason to believe that opianic acid and meconin contain the same quantity: a conclusion which accords with the existence of three atoms of methyl in narcotine and of one atom of the same radicle in cotarnine. Hence, opianic acid and its derivatives, must be respectively regarded as the dimethylised derivatives of the following still unknown normal compounds:—

Normal meconin	$\overline{C}_8H_6\overline{O}_4$,
Normal hydrate of meconin	$\overline{C}_8H_8\overline{O}_5$,
Normal opianic acid	$\overline{C}_8H_6\overline{O}_5$,
Normal hemipinic acid	$\overline{C}_8H_6\overline{O}_6$.

Of the whole group of substances, hemipinic acid is the one whose characters are best marked, and whose function is hitherto best known. We shall, therefore, in the first place endeavour, by tracing its analogies, to arrive at a probable rational formula for it, and then to deduce therefrom, formulæ for the other members of the group.

Hemipinic acid being, as Anderson has proved, a well-marked bibasic acid, the normal acid, from which we have supposed it to be derived by the substitution of $(\overline{C}H_3)_2$ for H_2, must contain altogether four atoms of replaceable hydrogen; further, two of these atoms of hydrogen must be susceptible of replacement by

the ordinary processes of saline double decomposition, but the other two must be so combined as to be unaffected by the same processes; in other words, normal hemipinic acid must be tetratomic but bibasic, and the two atoms of methyl contained in hemipinic acid, must occupy the place of the two non-saline replaceable atoms of hydrogen in the normal acid. According to this view, normal hemipinic acid would be comparable to lactic acid, which is diatomic but monobasic, and hemipinic acid itself would be comparable to the ethyl-lactic acid of Butlerow and Wurtz; a compound in which the ethyl is combined in such a way as to resist the processes of decomposition to which ordinary compound ethers yield: so that the former of the two last-mentioned chemists at first regarded ethyl-lactic acid as a true homologue of lactic acid, and described it under the name valero-lactic acid, until he found that its ethyl, like the methyl of hemipinic acid, is immediately eliminated by the action of boiling hydriodic acid. These relations of hemipinic acid and the supposed normal acid may be expressed by the following rational formulæ:—

Normal hemipinic acid .... $\left.\begin{matrix}(C_8H_2O_2)^{iv}\\(H_2)H_2\end{matrix}\right\}O_4$*,

Hemipinic acid ..... $\left.\begin{matrix}(C_8H_2O_2)^{iv}\\(CH_3)_2H_2\end{matrix}\right\}O_4$.

Adopting these formulæ and following the analogies that have been already pointed out, we may give to the other members of the opianic acid group the following rational formulæ:—

Hypothetical Normal Compounds.		Dimethylised Compounds.	
$\left.\begin{matrix}(C_8H_4O)^{iv}\\H_4\end{matrix}\right\}O_4$	.....	$\left.\begin{matrix}(C_8H_4O)^{iv}\\(CH_3)_2H_2\end{matrix}\right\}O_4$	Hypothetical hydrate of meconin.
$\left.\begin{matrix}(C_8H_4O)^{iv}\\H_2\end{matrix}\right\}O_3$	.....	$\left.\begin{matrix}(C_8H_4O)^{iv}\\(CH_3)_2\end{matrix}\right\}C_3$	Meconin.
$\left.\begin{matrix}(C_8H_2O_2)^{iv}\\H_3\end{matrix}\right\}\begin{matrix}H\\O_3\end{matrix}$	.....	$\left.\begin{matrix}(C_8H_2O_2)^{iv}\\(CH_3)_2H\end{matrix}\right\}\begin{matrix}H\\O_3\end{matrix}$	Opianic acid.

According to these formulæ, hydrate of meconin would be derived from a monobasic tetratomic acid by the replacement of two of the non-saline atoms of hydrogen by methyl, and would

* This acid would bear the same relation to terephtalic acid, $C_8H_6O_4$ (isomeric with normal meconin), that tartaric acid, $C_4H_6O_6$, bears to succinic acid, $C_4H_6O_4$, so that hemipinic acid may be regarded as dimethyl-dioxyterephtalic acid.

therefore itself still be a monobasic acid. Some evidence of the existence of such a compound is perhaps afforded by the fact that when the product obtained by heating opianic acid with potash is dissolved in water and the solution is made acid with hydrochloric acid, no meconin is precipitated at first, unless hydrochloric acid has been added in great excess; and also, that when meconin is heated to 100° in a sealed tube with aqueous ammonia, a solution is formed, from which the excess of ammonia can be removed by evaporation over sulphuric acid, without causing the meconin to separate, and which then gives with acetate of lead a precipitate containing meconin combined with oxide of lead.

Meconin, according to the above formulæ, must be regarded as a half-anhydride of this dimethylised acid, formed from it by the separation of two atoms of hydrogen, one of which is the saline atom, and an atom of oxygen.

Opianic acid is represented above as derived from a quarter-aldehyde (or hydro-trihydrate) corresponding to normal hemipinic acid, of which the full aldehyde would be

$$(\overset{\text{iv}}{\text{C}}_8\text{H}_2\text{O}_2).\text{H}_4.$$

Thus viewed, it may be compared with salicylous acid, a body formulated by Kekulé as half aldehyde and half acid; namely,

$$\left.\begin{matrix}(\overset{\prime\prime}{\text{C}}_7\text{H}_4\text{O}) \\ \text{H}\end{matrix}\right\rbrace \begin{matrix}\text{H}. \\ \text{O}\end{matrix}$$

4. The experiments described in this paper prove that cotarnine is a monomethylised compound, and hence there must exist, although it has not yet been isolated, a corresponding normal cotarnine $\text{C}_{11}\text{H}_{11}\text{NO}_3$, bearing the same relation to cotarnic acid that malimide does to malic acid. We may therefore compare cotarnine and its derivatives as follows:—

Cotarnic acid	$\text{C}_{11}\text{H}_{12}\text{O}_5$,
Cotarnamic acid	$\text{C}_{11}\text{H}_{13}\text{NO}_4$,
Hydrochlorate of cotarnamic acid	$\text{C}_{11}\text{H}_{13}\text{NO}_4.\text{HCl}$,
Cotarnimide (hypothetical normal cotarnine)	$\text{C}_{11}\text{H}_{11}\text{NO}_3$,
Methyl-cotarnimide (cotarnine)	$\text{C}_{11}\text{H}_{10}(\text{CH}_3)\text{NO}_3$.
Malic acid	$\text{C}_4\text{H}_6\text{O}_5$,
Aspartic acid	$\text{C}_4\text{H}_7\text{NO}_4$,
Hydrochlorate of aspartic acid	$\text{C}_4\text{H}_7\text{NO}_4.\text{HCl}$,
Malimide	$\text{C}_4\text{H}_5\text{NO}_3$,
Phenyl-malimide	$\text{C}_4\text{H}_4(\text{C}_6\text{H}_5)\text{NO}_3$.

Cotarnic acid, like malic acid, contains five atoms of oxygen, and is bibasic; hence it may be presumed to resemble malic acid in constitution. This acid, however, has been shown by the experiments of Perkin and Duppa, Kekulé and Schmitt, to be triatomic; and if we accordingly regard cotarnic acid as also triatomic, we get the following rational formulæ for it and its congeners:—

Cotarnic acid..... $\left.\begin{matrix}(C_{11}H_9O_2)'''\\H_3\end{matrix}\right\}O_3$,*

Cotarnamic acid ..... $\left.\begin{matrix}(C_{11}H_9O_2)'''\\H_4\end{matrix}\right\}\begin{matrix}O_2\\N\end{matrix}$,

Hypothetical normal cotarnine $\left.\begin{matrix}(C_{11}H_9O_2)'''\\H_2\end{matrix}\right\}\begin{matrix}O\\N\end{matrix}$,

Cotarnine..... $\left.\begin{matrix}(C_{11}H_9O_2)'''\\CH_3,H\end{matrix}\right\}\begin{matrix}O\\N\end{matrix}$.

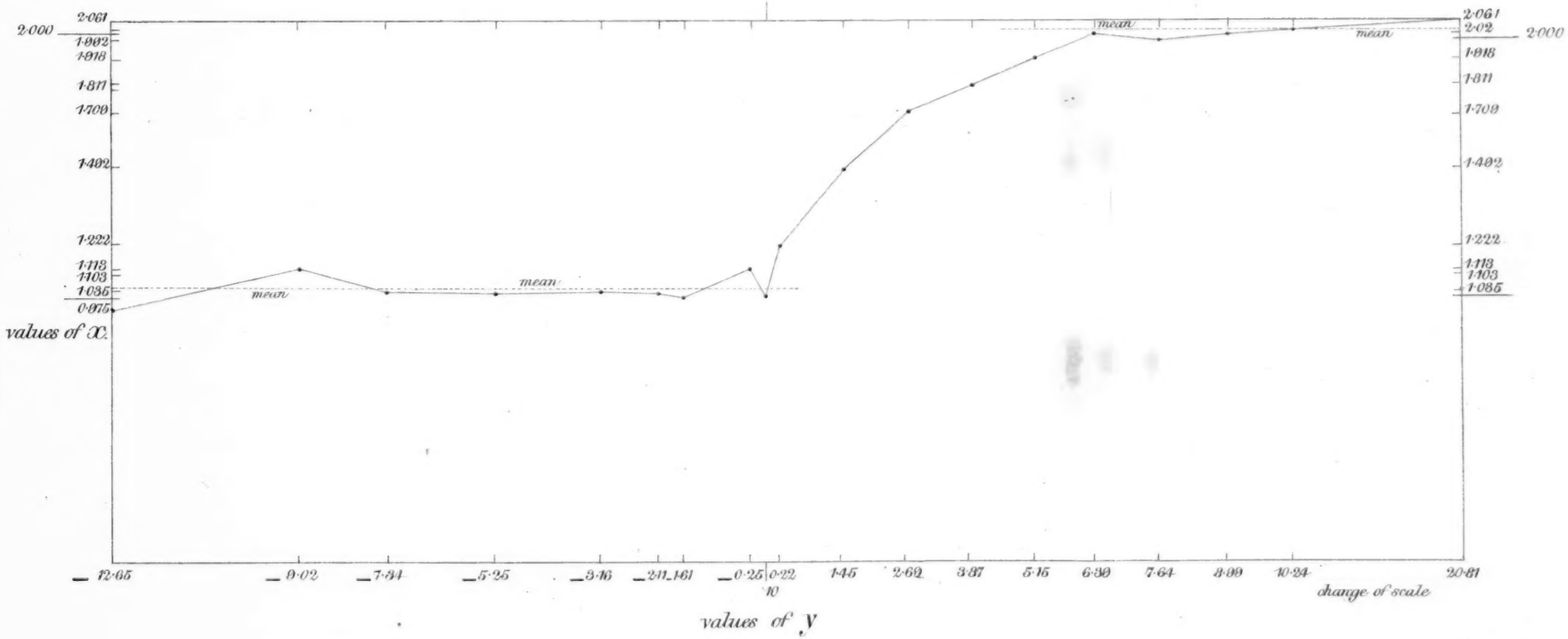
5. Combining this formula for cotarnine with that previously deduced for meconin, we arrive ultimately at the following expression as the rational formula of narcotine:—

$$\left.\begin{matrix}CH_3\\(C_{11}H_9O_2)'''\\(C_8H_4O)^{iv}\\(CH_3)_2H\end{matrix}\right\}\begin{matrix}N\\O\\O_3\end{matrix}$$

by help of which we believe that all the known transformations of narcotine may be accounted for, and a probable explanation given of the constitution of all its known derivatives. We will only further remark, with respect to this formula, that the primary hydrocarbons from which the radicles $(C_8H_4O)^{iv}$ and $(C_{11}H_9O_2)'''$ are respectively derived, are C_8H_{10} and $C_{11}H_{16}$, both of them homologous with benzene, C_6H_6, and the former either isomeric or identical with xylene.

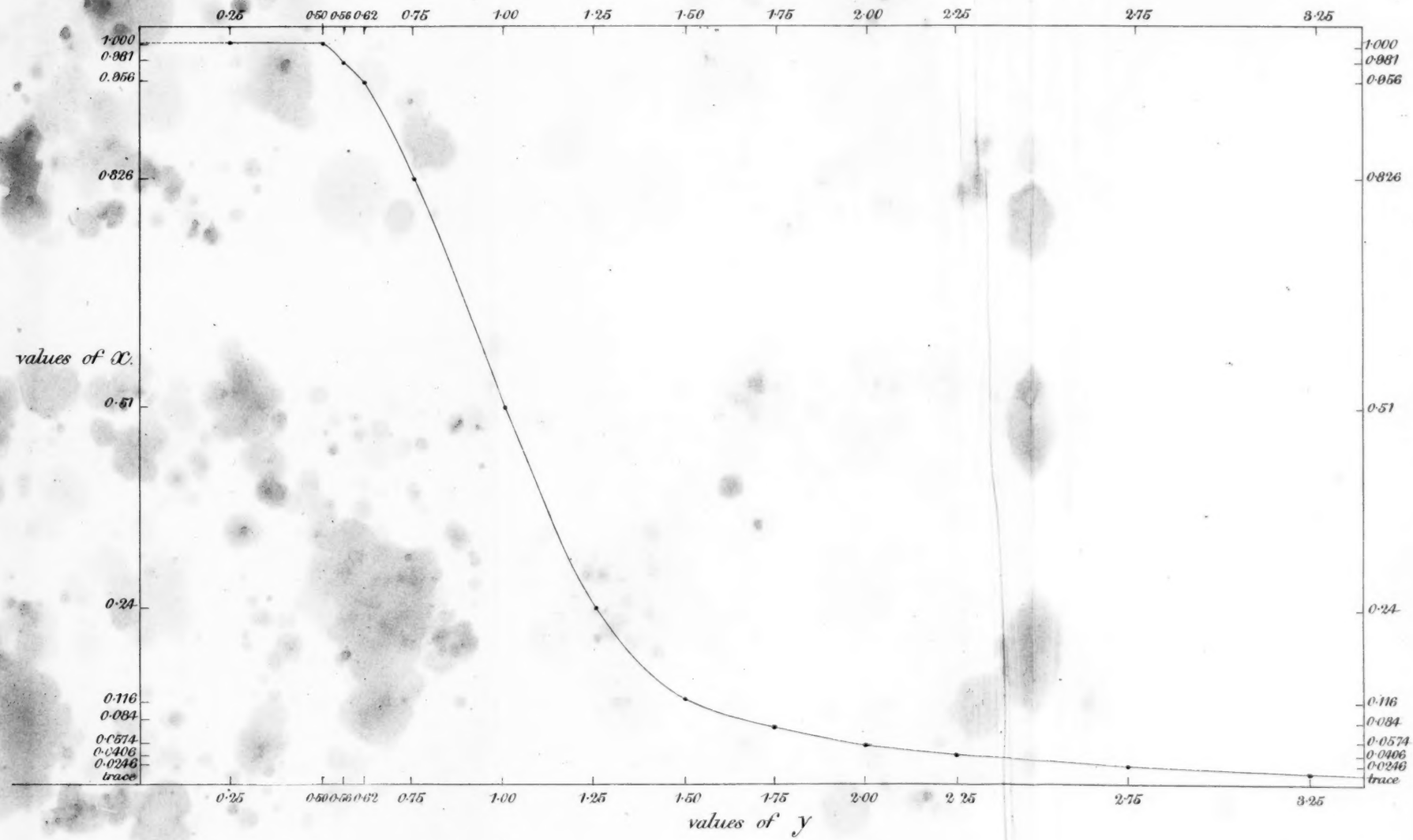
* Cotarnic acid appears to be homologous with Müller and De la Rue's *oxyterephtalic acid*, $C_8H_6O_5$, and, in respect to composition at least, it bears the same relation to Rossi's *homocuminic acid*, $C_{11}H_{14}O_2$ (*Compt. rend.* lii, 403) that malic acid bears to butyric acid. Oxyterephtalamic acid, $C_8H_7NO_4$, resembles its homologue (?) cotarnamic acid in combining with acids as well as with bases.

Curve of the decomposition of Chromic acid by Peroxide of Hydrogen.

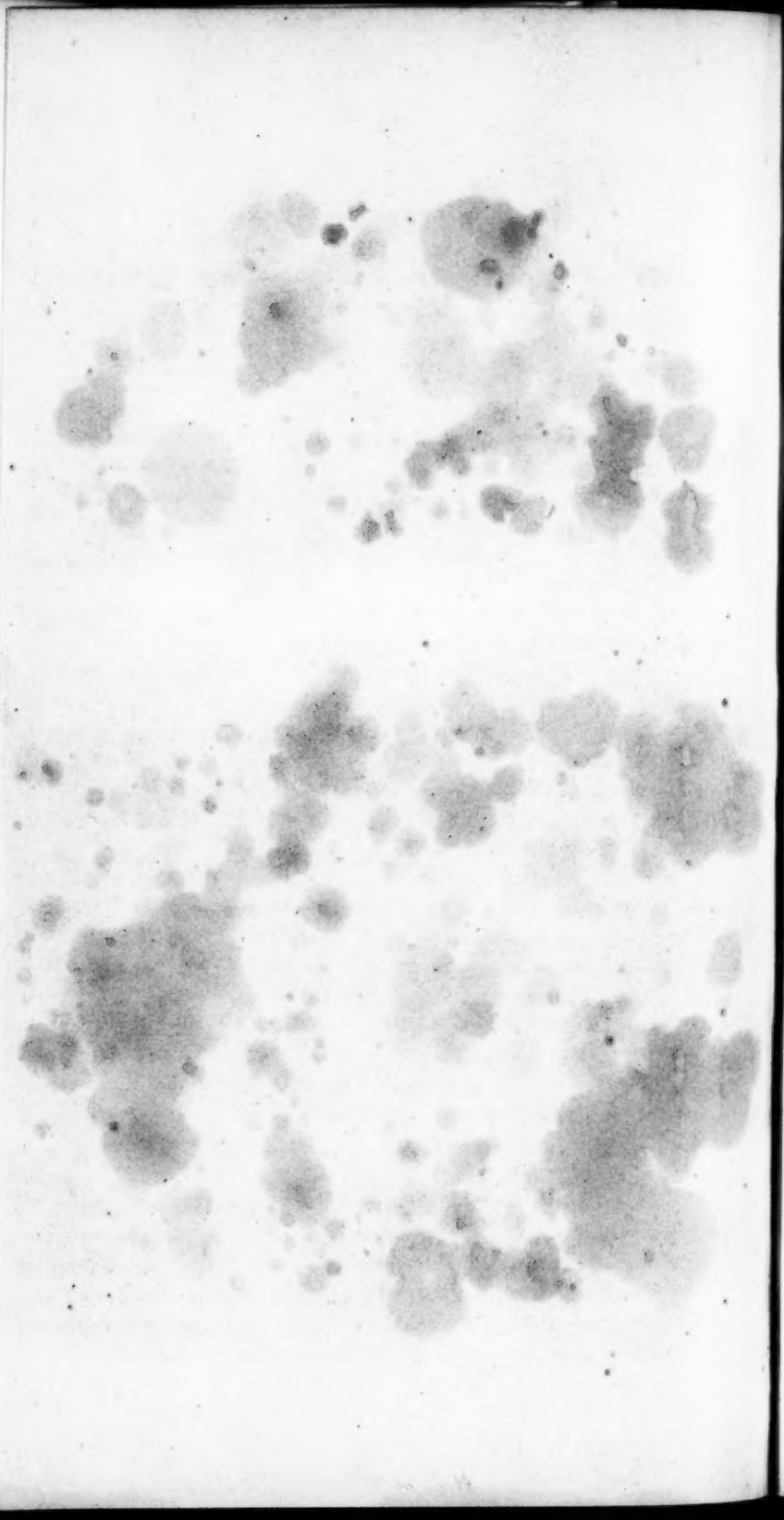


Harrisons, lith.

Curve of the decomposition of Hydrochloric acid by Peroxide of Hydrogen



Harrisons, lith.



XLIII.—*On the Properties of Electro-deposited Antimony.*

By George Gore, Esq.

Whilst engaged in depositing antimony by the electro-process, in October, 1854, I observed a singular development of heat by the deposited metal when scratched or rubbed, and published a brief account of it in the Philosophical Magazine, for January, 1855. I afterwards investigated the phenomenon more fully; and the following account, condensed from the Transactions of the Royal Society, contains all the leading facts relating to it.

When a current of electricity from two or three small elements of Grove's or Smee's battery is passed, by means of an anode of antimony and a cathode of copper, silver, or platinum, through a solution of terchloride of antimony, there is generally deposited upon the cathode a bright black amorphous metallic coating, which, if scratched by a needle or touched by a heated wire, instantly rises in temperature several hundred of Fahrenheit's degrees, sometimes with explosive violence, and evolves a small quantity of acid fumes.

If, instead of the terchloride solution, a solution of either terbromide or teriodide of antimony is employed, the deposited coating possesses somewhat similar properties, but in a much less conspicuous degree, especially the deposit from the teriodide. And if a solution of fluoride of antimony is employed, the deposited metal is of a grey colour, perfectly crystalline, and entirely destitute of the peculiar heating property. Under some circumstances, this crystalline variety of deposit may also be obtained by electrolysis from a weak solution of terchloride of antimony, especially if the battery power is very feeble, or the liquid is employed in a dilute or heated state.

The best solution for forming the strongly thermic variety of deposit is composed of one avoirdupois ounce of teroxide of antimony, or oxychloride of antimony, dissolved in five or six ounces of hydrochloric acid of sp. gr. 1·12; or it may be made by saturating two measures of hydrochloric acid with oxide or oxychloride of antimony, and then adding one measure more of the acid.

In common with electro-deposits generally, the inner and outer surfaces of both the black and grey deposits are in unequal states of cohesive tension, frequently in so great a degree as to rend the deposit extensively, and raise it from the cathode in the form of a curved sheet, with its concave side towards the anode. This state of tension is most manifest with rapidly formed thin deposits, especially upon extended flat surfaces.

It is worthy of notice that if the speed of deposition was *gradually* diminished to about 0·5 grain per square inch of cathode per hour, when it attained a certain degree of slowness (about 0·7 grain per square inch per hour), the character of the metal depositing *suddenly* changed from the amorphous black to the crystalline grey variety, without exhibiting the slightest gradation between; and the two layers of active and inactive metal might be readily separated by means of a knife. With deposits *very rapidly* formed, the fractured surface was coarse and less black, and the thermic change was found to be very strong, shattering the metal with almost explosive violence.

Faint crackling sounds frequently issued from the depositing metal, evidently caused in most instances by the cohesive action just mentioned; but in other cases they were due to the sudden expulsion of bubbles of gas from holes in the deposited metal, especially with the bromide variety, or by depositing upon an iron cathode in the terchloride solution. The deposit obtained in the bromide solution was frequently perforated with holes all over its surface, and had the appearance of a metallic sponge, caused by the numerous bubbles of gas.

The thermic property of the deposit from the terchloride gradually disappears; the substance in a state of powder loses its power in six months; fragments, $\frac{1}{16}$th of an inch thick, lose their power in the course of twelve months; whilst others, $\frac{1}{4}$th of an inch thick, still possess a portion of their heating power at the end of three or four years.

Each of the varieties of active antimony is fragile and easily broken; that from the iodide solution is extremely so. Thin pieces, $\frac{1}{16}$th of an inch thick, of the chloride variety may be broken in the air at 60° Fahr. without discharging their heat, if broken with care; thicker pieces should be broken under the surface of cold water, by gentle blows with wood or other substance not very hard. Very thin pieces may with care be reduced to fine powder in a mortar, under a mixture of ice and water; and the powder so

produced, after drying in a slightly warm place, possesses all the heating property of the original solid mass.

Heating the chloride variety to 212° Fahr. for one hour in boiling water, or keeping it at somewhat lower temperature (185° or 190° Fahr.) for a longer period in an air-bath, causes it *gradually* to evolve its heat and lose its peculiar heating power.

A cylindrical bar of the chloride variety, about $\frac{1}{2}$ an inch in diameter, formed upon a rod of grain tin $\frac{1}{8}$th of an inch thick, when changed by the momentary contact of a heated wire, evolved sufficient heat to melt the tin completely, and the tin ran out through a crack in the antimony, and remained liquid a short time.

By applying momentary heat to the ends of deposits formed upon heliacal copper wires, the action was gradually transmitted to the opposite ends at a speed varying from twelve to thirty feet per minute, the rapidity of progress depending chiefly on the absence of cooling influences, cracks in the metal, and grey crystalline deposit. The progress of the change was rendered visible by the evolution of a small cloud of vapour at its advancing point, and by a peculiar snake-like movement in the coils at that part, apparently produced by the cohesive change in the deposit. With massive deposits the speed of transmission would doubtless be much greater.

The specific gravity of the active chloride variety varied from 5·739 to 5·944; but after having been discharged suddenly of its heat, its specific gravity varied from 5·748 to 6·029. The specific gravity of the inactive or crystalline variety varied from 6·369 to 6·673.

Their electro-chemical equivalents, determined by electrolysing their solutions simultaneously with a solution of sulphate of copper, and weighing the deposits, were 42·30 to 43·81 parts of the active variety, and 40·41 to 40·79 parts of the crystalline kind, for every 31·7 parts of copper deposited in the copper solution.

The peculiar change in the active chloride variety is attended by alterations in the colour, cohesion, and fractured surfaces of the substance; from a bright steel colour and glassy fracture, it passes to a dull grey colour and granular fracture, and its cohesive power greatly increases. These changes occur whether the heat has been evolved suddenly, or very gradually by long lapse of time. Similar effects are observed, but in different degrees, with the bromide and iodide deposits. Straight bars of the active chloride variety suddenly discharged, become curved by the heat, the outer side or

that last deposited invariably becoming concave; this is similar to the effect of heat upon electro-deposited metals generally.

The heat evolved by the peculiar change in the chloride variety is not due to cohesive action; for it has been found that the amounts of heat evolved by similar weights of the substance in a single solid mass, in small pieces, and in fine powder, in a calorimeter, were not sensibly different. Nor is the heat due to alteration of the specific heat of the substance during the change. The specific heats and gravities of several bars of the active substance were determined; the bars were then suspended in an air-bath at about 185° Fahr., or in boiling water, until their heat had all been *gradually* evolved, which occupies about half-an-hour in the water; their specific heats and gravities were then redetermined and found to be scarcely at all altered. With similar bars and pieces *suddenly* discharged, the specific heat decreased from 0·0631 to 0·0543, and the specific gravity increased; the reason being, that by the *sudden* discharge they had been heated to a much higher degree, and the greater degree of heat had expelled a much larger proportion of the inclosed chloride of antimony, which the *amorphous* chloride variety always contains.

The temperature to which the active chloride variety must be raised either locally or throughout its mass, to produce the *sudden* discharge, varies according to several circumstances, but is generally about 200° or 210° Fahr., in an air-bath. The discharge is not limited to one particular temperature, but commences between 170° and 190°, and gradually increases in rapidity by rise of temperature to some point about 200° or 210° Fahr., when it attains its maximum, and discharges all its remaining heat suddenly. When the amount of cooling influences is great in relation to the amount of heat to be discharged, and the heat is conveyed away as fast as it is set free, as by immersion of the substance in boiling water, and the substance therefore never attains so high a temperature as when heated to 200° or 210° Fahr. in the air, the discharge of heat and the change of state of the substance is *gradual*, and may be made even fragmentary by repeated brief immersions in the boiling water. A rod of the substance may be gradually discharged of its heat at one end, without discharging the opposite end, by immersing that end for one hour in nearly boiling water.

The total amount of heat evolved by the sudden discharge of the chloride variety was considerable, and was sufficient in most instances to raise the temperature of an equal weight of ordinary

antimony of specific heat 0·0508 about 650 or 700 Fahr. degrees, and in one instance 705·89 Fahr. degrees, above the atmospheric temperature (60° Fahr.) at which it was discharged.

When the active chloride variety is *suddenly* discharged of its heat, there is invariably evolved from it a small quantity (generally about 3·5 per cent.) of vapour, consisting almost entirely of terchloride of antimony. This evolution of vapour is not a *cause* but an *effect* of the heat; it does not occur when the temperature of the substance during discharge is not sufficiently high to volatilize the inclosed chloride, as when the substance is *gradually* discharged of its heat.

It is important to observe that the amount of heat evolved by this sudden change of antimony is different at different temperatures, and is greater at high temperatures than at low ones. A bar cooled to 34·0° Fahr. and discharged, evolved sufficient heat to raise the temperature of its own weight of ordinary antimony (specific heat = 0·0508) 638 Fahr. degrees; whilst a similar one, heated to 157° Fahr. and discharged, evolved sufficient heat to raise its own weight of ordinary antimony 732·8 degrees.

The grey or crystalline variety of deposited antimony is generally very free from impurities, and from the constituents of the depositing liquid; whilst the amorphous or active kind contains small portions of all the constituents of the electrolyte, and invariably contains about 6 or 6½ per cent. of terchloride of antimony.

The following are the results of two analyses of specimens obtained from a pure solution of the chloride:—

No. 1.			No. 2.		
Sb ..	93·36		Sb ..	93·51	
$SbCl_3$ ..	5·98	= 6·44	$SbCl_3$ ..	6·03	= 6·24
HCl ..	0·46		HCl ..	0·21	
	99·80			99·75	

If a quantity of the active variety in a state of fine powder is kept in a closed bottle for twelve months and then examined, it is found to emit a slightly acid odour, and to have lost all its heating power; similar results occur if a flask containing some active powder is immersed in boiling water for an hour.

Equal quantities of active powder and powder gradually discharged of its heating power, were digested at 60° Fahr. with

dilute hydrochloric and tartaric acid for two days; the discharged powder was then found to have yielded to the dilute acid, by solution, about twice the quantity of its chloride of antimony that the other had yielded; showing that, with the loss of heating power, there occurs a diminished degree of union between the deposited metal and its associated chloride of antimony.

It would appear that the heating power is closely dependent upon the presence of the associated chloride: for in every instance where the chloride was extracted, by digesting the powder at 60° Fahr. for weeks or months in various solvents, the heating power disappeared.

There are no circumstances at present known under which the substance retains its heating power unimpaired by lapse of time.

The foregoing remarks apply chiefly or nearly wholly to the variety of active deposit obtained in a solution of terchloride of antimony, because that variety is the most readily obtained, the most powerful in its action, and the most definite in its results.

The second variety of active antimony may be obtained as follows: Dissolve one part of teroxide of antimony in 10 parts of hydrobromic acid of specific gravity about 1·3; filter the solution, and electrolyse it by means of three Smee's elements and an anode of antimony, at a speed of deposition of about 3 to 5 grains per square inch of receiving surface per hour.

This variety is of a lighter colour than that from the chloride, and is generally quite dull in aspect. It exhibits less of the cohesive cracking action than the first kind, and is less hard. Its specific gravity at 60° Fahr. varies from 5·415 to 5·472.

By momentary contact of a red-hot wire, it exhibited a similar molecular and thermic change, but the action did not spread throughout the mass unless it was previously raised to a temperature of about 250° Fahr.; if then touched with the wire, it evolved all its heat instantly with explosive violence and projection of pieces of the substance. Scratching the heated substance by a steel pointer did not cause it to discharge its heat. Pieces heated upon mercury or melted fusible alloy, discharged themselves suddenly and powerfully when the bath attained a temperature of about 320° Fahr.

Thick pieces may be easily reduced to powder in a mortar without causing a discharge of heat. A train of the powder heated upon a platinum dish in a bath of chloride of calcium at 265° Fahr., and touched at one end by a red-hot wire, discharged its

heat gradually, and the change, attended by evolution of fumes, was slowly propagated to the distant extremity.

This variety was *gradually* discharged of its heat by placing it upon the surface of mercury at 260° Fahr. for one hour; or by suspending it during 30 minutes in a solution of chloride of calcium at 252° Fahr. During this latter period it lost 6·117 per cent. in weight.

By fusion in a bent tube of refractory glass, it was found to consist of 79·52 per cent. of metal and 20·48 per cent. of volatile matter, a colourless buttery substance, slightly semifluid at 60° Fahr., which doubtless consisted of terbromide of antimony and a little aqueous hydrobromic acid. Other specimens treated thus gave respectively 18·42 and 20·40 per cent. of volatile matter; the two specimens being parts of a single deposit, the first being from the upper and the second from the lower part of the deposit as it was suspended in the electrolyte.

The electro-chemical equivalent of this variety was determined by depositing it simultaneously by the same current with the chloride variety; and ascertaining the relative weights of the two deposits. In two experiments of this kind there were obtained respectively 50·09 and 50·11 parts of this variety for every 42·5 parts of the active chloride variety, or 32·2 parts of zinc consumed. And in two other determinations 51·2 and 51·4 parts of bromide deposit were obtained. Each of these quantities of deposit contained the same amount of *metallic* antimony, viz., 40 parts, or ⅓rd of an equivalent; the remainder being the associated salt of antimony. The variation in the numbers of the bromide deposit probably arose from absorption of moisture caused by its porosity.

After gradual discharge, the cohesion of this variety, like that of the previous kind, was found to be greatly increased, its fractured surface became less metallic, and was dull and earthy in appearance; reduced to powder, it strongly reddened damp litmus paper, whilst the powder of the unchanged substance did not; the odour and taste of the changed substance were also acid. These results indicate that the change and evolution of heat is attended by a diminished degree of attraction between the metal and its associated saline or acid matter, similar to the change in the chloride variety.

The third variety of heat-giving electro-deposited antimony was obtained as follows: Dissolve one part by weight of teroxide of antimony in fifteen parts of hydriodic acid of specific gravity 1·25,

and electrolyse it at a speed not exceeding one grain per square inch of cathode per hour.

The deposit is scaly-grey, dull in appearance, very friable, and much less metallic in character than either of the other kinds, unless it has been deposited with extreme slowness. The specific gravity of a slowly-formed specimen was 5·27. On immersing dry pieces in water, a hissing sound, as of strong absorption, occurred, and numerous bubbles of gas issued from all parts of its surface during a few seconds. The tendency to evolution of hydrogen gas in the solution is so great as frequently to disintegrate the deposit completely.

Pieces 1-9th of an inch thick required to be heated upon mercury to 338° Fahr. before the contact of a red-hot wire would cause a discharge of heat; it then discharged but feebly, with evolution of red vapours of iodide of antimony. A similar piece heated upon mercury discharged itself feebly when the mercury attained a temperature of 350° Fahr.; the action was slow, and occupied about twenty seconds. By exposure to strong sunlight, during two hours, this variety acquires externally a reddish-brown colour.

By fusing the unchanged substance in a glass-tube, it yielded 77·76 per cent. of metal, and a solid, red, easily fusible sublimate, together with a little moisture, evidently teriodide of antimony, and a little aqueous hydriodic acid.

Its electro-chemical equivalent was determined in the same way as the previous kind. With slow action (0·5 grains per square inch of cathode per hour) 50·39 parts of deposit were obtained; and with very slow action (0·2 grain per square inch per hour) 48·07 parts were obtained for every 42·5 parts of deposit in the chloride solution.

The following are some recapitulations, with comparisons of the three active varieties. The solution for obtaining each requires an excess of free acid, greatest with the chloride, and least with the iodide. The rate of deposition admissible to obtain firm deposits, is greatest with the chloride, and least with the iodide. The phenomenon of unequal cohesion and cracking is exhibited most in the chloride variety, and least in the iodide. The chloride deposit is the most metallic in appearance, and has the strongest cohesion; the iodide is the least metallic, and has the weakest cohesion. The specific gravities of the deposits are also in series; that from the chloride is 5·8, from the bromide 5·44, and from the

iodide 5·25. The temperatures of sudden discharge are, for the chloride variety, about 200° Fahr.; the bromide, about 280° Fahr.; and the iodide, about 340° Fahr. The manifestation of heat is great in the chloride deposit, less in the bromide, and least in the iodide. They each become less metallic in appearance by the thermic discharge, and acquire increased cohesion. The chloride variety contains about 6·3 per cent. of saline matter, the bromide about 20, and the iodide about 22·2. The pseudo-electro-chemical equivalents of the deposits, which depend upon the amount of saline matter united to an equivalent of metallic antimony in them, is about 42·5 for the chloride variety, 50 for the bromide, and 51 for the iodide.

In conclusion I beg to submit the following remarks respecting the formation and properties of these substances:

The electric current in passing decomposes the salt of antimony, setting free 1 eq. of chlorine, bromine, or iodine, and $\frac{1}{3}$rd of an eq. of antimony for every single equivalent of zinc consumed. The antimony in the act of depositing, being in what is termed the "nascent state," unites chemically, in a comparatively feeble or unstable manner, with the ingredients of the electrolyte, combining with them in a somewhat variable proportion. The $\frac{1}{3}$rd eq., or 40 parts of antimony, carry down about $2\frac{1}{2}$ or 3 parts from the chloride solution, about 10 parts from the bromide liquid, and about 10·5 parts from the iodide solution, and thus occasion about 42·75 parts of deposit in the first liquid, 50 parts in the second, about 50·5 parts in the third solution, for each equivalent of zinc consumed. I have ventured to call those numbers the pseudo-electro-chemical equivalents of the deposits to distinguish them from the true equivalent of antimony which they disguise.

Another explanation, which has nearly an equal weight of evidence in its favour, is that the antimony is deposited in the *amorphous* state, and the chloride or other salt is inclosed mechanically in it during the process of deposition, and that the change consists in the assumption by the metal of the crystalline state, whereby it is converted into an inconceivable number of crystals of insensible size, and the imprisoned salt is set free.

Antimony is not the only metal that manifests this property of uniting during electrolysis with ingredients of the electrolyte; silver deposited from a cyanide solution containing a small quantity of bisulphide of carbon, retains a small proportion of some of the

ingredients of the electrolyte, and possesses very different properties from silver deposited from other cyanide solutions. It would be desirable to examine further the conditions which regulate this species of combination, and that influence the proportions of the substances which unite by it. In the case of antimony, the combination is evidently dependent upon the rate of deposition; for when the speed in the chloride solution fell below about 0·75 or 0·5 grain per square inch of cathode per hour, the antimony lost its power of combining with the antimonial salt, and was deposited alone in the grey or crystalline state. It is also dependent upon the temperature of the liquid, and upon the proportions of the ingredients of the solution. In an experiment already mentioned, the proportion of antimony that united with the bromide of antimony, varied with the depth of immersion of the cathode in the depositing liquid.

Either of the active varieties of antimony may be viewed as a feeble chemical compound of metallic antimony with a salt of antimony; that it is not a purely mechanical mixture is rendered probable by the fact of its powder not reddening moistened litmus paper, especially in the case of that obtained from the bromide solution, which contains as much as 20 per cent. of saline and acid matter, whereas, immediately after the gradual change has occurred, it has the power of reddening litmus strongly, and the salt of antimony contained in it may then be much more readily extracted by dilute hydrochloric or tartaric acid. These facts also indicate that the change is, at least in part, a case of chemical decomposition, the substances remaining together after the decomposition in a state of mechanical mixture.

The compound deposited is evidently not a *direct* result of electrolysis, otherwise it would be deposited in the proportion of its electro-chemical equivalent; nor is it a *definite* chemical compound, because there is no equivalent or atomic proportion between the quantity of metallic antimony and that of the salt with which it is combined, and because the proportions of these two ingredients appear to be in each case somewhat variable.

Numerous electrolytic experiments were made with solutions of arsenic, and small portions of scaly deposit from the aqueous fluoride appeared to exhibit in a feeble degree (like the third variety of active antimony) a thermic property similar to that of electro-deposited antimony.

XLIV.—*On the Chinoline and Leukoline Series.*

By C. Greville Williams, F.R.S.

In a paper recently presented to the French Academy of Sciences, Dr. Hofmann has given the results of an elaborate investigation of iodide of pelamine, or chinoline blue, a substance discovered by me some years ago while making a comparative study of the isomeric bases of the chinoline and leukoline series. The publication of that paper renders it desirable that I should lay before the Society a brief account of the results which I have obtained, although they are, as yet, far from complete. I reserve the analytical details until the publication of the entire investigation.

My analysis of the prisms of iodide of pelamine gave results agreeing with Hofmann's formula. It is due to Dr. Hofmann to state that he was the first to arrive at the true formula of the iodide, as I had allowed my experiments to drift into other channels, and had more especially followed up the study of the other products of the reaction of iodide of amyl on chinoline and lepidine.

I have not accepted the term "cyanine," which has been given in France to the base contained in the blue substance, because such a name would lead to incorrect views as to its derivation.

There are some curious secondary reactions which take place in the preparation of the iodide of amyl-lepidyl-ammonium, which do not appear to have been noticed by other observers. On cohobating iodide of amyl with lepidine, a brown syrup-like fluid is obtained, which solidifies, on cooling, to a mass of crystals. On repeatedly boiling out this mass with water, the greater part dissolves, yielding a solution of the iodides of the ammonium bases, from which iodide of pelamine may be obtained by boiling with alkalies. A considerable portion, however, remains undissolved. This insoluble portion, on prolonged ebullition in a retort with caustic alkalies, decomposes, yielding a distillate consisting of water and an oil. The latter, on treatment with hydrochloric acid, for the most part dissolves, allowing a very small portion of iodide of amyl to separate. The hydrochloric solution, on evaporation to a moderate bulk, forms two layers; the upper, which appears like a colourless oil, solidifies on cooling to a mass resembling paraffin. The lower portion is merely a saturated aqueous solution of the same substance. The paraffin-like hydrochlorate, on treatment with alkalies and subsequent distillation, yields a remarkable

volatile base, which may be dried for analysis by digestion with sticks of hydrate of potassium. When perfectly dry it distils at about 275° C. By rectification it may be obtained nearly colourless. Its odour is fragrant, and recalls that of the higher monamines of the amylic class. I was at first inclined to regard it as triamylamine, and, in fact, a small portion of that base is present in the oil, and renders fractional distillation necessary.

On combustion of the least volatile portion, it yielded numbers agreeing perfectly with the formula

$$\mathrm{C_{20}H_{32}N_2}.$$

Further investigation has shown that this formula should be written:—

$$\left.\begin{matrix}\mathrm{C_{10}H_{23}N}\\ \mathrm{C_{10}H_9N}\end{matrix}\right\}$$

It is, therefore, biamylamine coupled with lepidine in the same manner that paraniline is aniline coupled with itself.

So singular a constitution requires to be supported by the strongest evidence, and I was consequently very desirous of ascertaining the density of the vapour. Unfortunately the quantity of substance in my possession was so small that I could not spare sufficient for an experiment, by the method of Dumas, on the usual scale, and the boiling point was far too high for the ordinary process of Gay Lussac. I, nevertheless, made, with the most extreme care, an experiment in a very small balloon. The resulting number was 10·40, being almost absolutely the value required by the formula, namely 10·38.

The hydrochlorate of this base, which I provisionally call lepamine, fuses below 100°, the analysis agreed sufficiently with the formula

$$\mathrm{C_{20}H_{32}N_2,2HCl}.$$

It is but sparingly soluble in water, and requires to be rendered nearly dry *in vacuo*, before being exposed to the heat of the water-bath.

On adding a solution of bichloride of platinum to an aqueous solution of the hydrochlorate, a pitch-like mass is precipitated, and the solution gradually turns green, finally depositing an olive-green powder. On filtering, a clear yellow solution is obtained, but, on exposure *in vacuo* to a surface of sulphuric acid, the green substance is again deposited. If, however, an excess of strong hydrochloric acid be added to some of the base, so as to obtain

the hydrochlorate floating as an oil on the surface, and then considerable excess of a solution of bichloride of platinum be poured in, an adhesive mass of a yellow colour at once forms. It may be gathered to the side of the beaker so as to allow of the removal of the aqueous fluid by decantation. On stirring the product repeatedly with cold water, it may be effectually washed. It is then to be dried *in vacuo* over sulphuric acid for a day or two, after which the dessication may be finished in the water-bath without any signs of decomposition.

The platinum salt, as thus prepared, is almost entirely soluble in alcohol, showing the absence of lepidine, the platinum salt of which is insoluble in spirit.

In spite of its unpromising physical properties, the salt obtained from two distinct preparations gave, on ignition, almost exactly the theoretical numbers required by the formula—

$$C_{20}H_{32}N_2,2HCl,PtCl_2.$$

On adding a solution of terchloride of gold to a solution of the hydrochlorate, a chocolate-coloured precipitate falls at first, but it turns directly to a bright green; it is soluble in alcohol, forming a green solution.

Dissolved in strong nitric acid, the base affords a red solution, which, on dilution with water, allows a red oil to separate; it appears to be a nitro-compound.

On treating the base with iodide of ethyl in a sealed tube, a syrupy fluid is obtained, which on distillation with potash yields a volatile oily base. It dissolves readily in hydrochloric acid, affording a salt which appears to crystallise with far greater difficulty than the hydrochlorate of the parent base. The gradual replacement of the basic hydrogen in such an alkaloid as that under consideration will probably give interesting results.

In conclusion I may state that the fact of the coal and cinchonine bases being essentially distinct renders it necessary to slightly modify their nomenclature.

The base from coal $C_{10}H_9'''N$, which is isomeric with lepidine, I propose to call "iridoline," and the cinchonine base, isomeric with cryptidine, I have termed "dispoline." The two series will, therefore, stand thus:—

Coal series.		Cinchonine series.	
Leukoline ..	$C_9H_7'''N$.	Chinoline ..	$C_9H_7'''N$.
Iridoline ..	$C_{10}H_9'''N$.	Lepidine ..	$C_{10}H_9'''N$.
Cryptidine ..	$C_{11}H_{11}'''N$.	Dispoline ..	$C_{11}H_{11}'''N$.

I have fully satisfied myself that the chinoline series by no means ends with dispoline. I have already attained the platinum salts of the bases $C_{13}H_{15}'''N$ and $C_{14}H_{17}'''N$. These bases, as well as dispoline, are now under examination.

XLV.—*On some Amalgams.*

By J. P. Joule, LL.D., F.R.S., &c.

[Abstracted from the Memoirs of the Literary and Philosophical Society of Manchester, vol. ii., 3rd series.]

The experiments I am about to describe were made twelve years ago, but their publication was delayed to the present time in the hope of being able to extend them. Although I have not found an opportunity of doing so, I trust that these comparatively old observations will be deemed of sufficient interest to justify me in having submitted them to the Society.

My attention was first directed to the subject through my wish to discover a ready means of procuring a perfectly true and polished metallic surface. Since it was believed that mercury refused to enter into combination with iron,* I thought that by depositing the latter on mercury, a plate of it would be formed possessing a smoothness equal to that of the fluid metal. However, on making the experiment, I found that the iron entered into combination with the mercury, forming an amalgam.†

One element of a Daniell's battery was amply sufficient for the purpose. Its zinc plate was connected by a wire with a globule of mercury covered by a solution of sulphate of iron,

* I find that Sir John Herschel described the Amalgam of Iron in his Bakerian Lecture on the movements of Electrified Mercury, in the following words (Note on § 37):—"The amalgam of iron obtained in one experiment was a white friable solid, of lustre between silver and iron: the mercury being driven off by heat, the iron took fire, and glowed like a live coal till reduced to the state of black oxide, soluble in muriatic acid, having all its characters."—J. P. J., October, 1863.

† In consequence of iron possessing nearly the same affinity as hydrogen for oxygen, there is considerable difficulty in depositing it electro-chemically on a metallic plate. I have only once or twice obtained a good electrotype deposit on a polished surface, to which the iron adhered so firmly that it could only be removed by abrasion. Even in the process of amalgamating iron, the constant evolution of hydrogen from the mercury shows that decomposition of water takes place simultaneously with that of the salt of iron.

whilst an iron wire attached to its copper plate, and dipping into the solution, completed the circuit. The iron wire gradually dissolved, whilst an equal portion was taken up by the mercury, which, in doing so, by degrees lost its fluidity, until at length a mass of crystals of amalgam was formed having a greyish-white colour of metallic brilliancy. The time required to complete the operation was generally about one day; but a longer or shorter period was occupied in some instances, in consequence of variations in the quantity of mercury employed, and in the efficiency of the voltaic arrangement. The following Table contains the results of most of the experiments made on the amalgam of iron. The analysis of this and other amalgams was made by heating them in a glass tube through which a current of hydrogen was passed.

No.	Composition.		Sp. grav.	Remarks.
	Mercury.	Iron.		
1.	100	0·143	..	Perfectly fluid.
2.	„	1·39	..	Fluid.
3.	„	2·97	..	Semi-fluid.
4.	„	11·8	12·19	Soft.
5.	„	18·3	..	Solid: colour, greyish-white.
6.	„	47·5	..	Solid: good metallic lustre.
7.	„	127·6	10·11	Solid: friable.
8.	„	14·74	..	The superfluous mercury pressed out from the semi-fluid amalgam by hand.
9.	„	79	..	Compressed rapidly, and with a force of fifty tons on the square inch.
10.	„	103·2	..	Ditto.

No. 5 of the above Table was a solid amalgam of a greyish-white, approaching the colour of iron. It could be easily broken into powder. When dried and left undisturbed, it soon became covered with small globules of mercury, until ultimately it was entirely decomposed.

To obtain No. 6, I used a solution of chloride of iron instead of the sulphate which was used in all the other experiments.

No. 7 could be easily reduced to powder. It had a bluish colour, and was destitute of metallic lustre until it was rubbed. It remained some time under water without change, but when dried became speedily decomposed, whether it was exposed to the action of air, or was placed under the exhausted receiver of an air pump.

The amalgam of iron, whether solid or fluid, is attracted by the magnet, and in the solid condition is capable of receiving a slight dose of permanent magnetization.

In No. 1, the iron, though apparently completely dissolved by the mercury, remained in the full possession of its magnetic virtue.

A portion of No. 2, weighing 87·69 grains, placed in a piece of quill, was attracted by a magnet with a force equal to 0·36 gr. 3·058 grains of iron wire, cut into small pieces and placed in the same quill, were attracted by a force of 0·94 gr. The quantity of iron contained in the amalgam was 1·2 grain. Hence it appeared that the iron had lost very little of its magnetic virtue by combination with the mercury.

The following observations were made to discover the position of the amalgam of iron in the electro-chemical series. The galvanometer which was employed had a coil 1 foot in diameter, composed of 400 convolutions of wire 1-40th of an inch in diameter.

Positive Metal.	Negative Metal.	Deflection.
Amalgamated zinc.	Zinc.	10°
Zinc.	Iron.	42°
Zinc.	Copper.	65°
Amalgamated iron.	Copper.	15°
Iron.	Amalgamated iron.	5°

It appears, therefore, that the amalgamation of iron produces a contrary effect to the amalgamation of zinc. This is especially remarkable, as the amalgamated iron contained no carbon, which must have existed to a certain extent in the plate of iron with which it was associated.

When amalgam of iron is left under water for a few days, it becomes coated with rust. If shaken violently, it becomes almost immediately decomposed, the iron as a black powder floating on the surface of the liberated mercury.

When the amalgam is heated to the boiling-point of mercury, the liberated iron unites with the oxygen of the air, throwing off bright red sparks, and leaving a hard lump of oxide.

The experiments seem to indicate that the solid amalgam of iron which contains the largest quantity of mercury is a binary combination of the two metals.

The specimen marked No. 8 in the Table was procured by com-

pressing by hand between folds of linen a quantity of amalgam in a soft state. There resulted a mass of white crystals of perfect metallic lustre. The mercury left was about two equivalents. It seemed probable that one of these was left uncombined among the pores of the amalgam.

The specimens Nos. 9 and 10 were obtained by hydraulic pressure acting on a piston of steel 3-8ths of an inch in diameter, working in a cylinder into which a silken bag filled with amalgam was placed. The resulting amalgam was so hard, that it could only be broken by the smart blow of a hammer. Its black colour seemed to indicate nearly total decomposition.

Amalgam of Copper.—To form this amalgam, a small quantity of mercury was poured into a dish containing solution of sulphate of copper. A copper wire connected the mercury with the zinc of a Daniell's cell, whilst a coil of copper wire immersed in the cupreous solution completed the circuit. A mass of crystals was gradually formed, branching out to the distance of half an inch or more. Ultimately pure copper was deposited on the extremities of the crystals in a fringe of light red, the whole presenting the appearance of a beautiful flower. In the following Table I have collected the results of several such experiments :—

No.	Mercury.	Copper.	Sp. grav.	Remarks.
1.	100	22·5	13·32	Arborescent crystals : no pink deposit.
2.	„	24·73	13·260	Ditto ditto.
3.	„	25	13·185	Ditto ditto.
4.	„	27·76	13·17	Ditto ditto.
5.	„	29·92	....	Pink deposit on the extremities of the crystals.
6.	„	37·7	....	Pink deposit over the greatest part.
7.	„	31·35	13·51	The copper which was deposited on the outside of the crystals was constantly removed. The experiment was stopped when the central button of amalgam became pink in one or two places.
8.	„	29·08	....	Ditto ditto.
9.	„	29·0	13·76	Ditto ditto.
10.	„	34·19	13·01	From a hot solution of sulphate of copper. Hard and crystalline mass.
11.	„	39·64	12·99	Formed slowly in eight days. Pink in several places.
12.	„	41·5	....	This amalgam was continually pounded whilst it was being produced. Pink in several places.
13.	„	38·12	12·65	Sulphate of copper, kept at 100° Fahr. In two days the amalgam was covered with arborescent crystals tipped with pink.

On inspecting the above Table, it will appear that whenever the quantity of copper approaches nearly to an equivalent, a deposit of unamalgamated copper begins to take place. This seems to demonstrate that the solid amalgam containing the least quantity of mercury is a binary compound.

The mean of the specific gravities of the specimens possessing an equivalent (or a little less than an equivalent) of copper is 13·31.

The specific gravity of the other amalgams, containing excess of copper, is 12·82. It follows that, if we admit that the specific gravity of copper is not altered when it enters into combination with mercury, the specific gravity of the latter, in the amalgam, is 15·415.

In the following Table I give the analysis of amalgams after pressure of various degrees of force had been applied during various lengths of time:—

No.	Pressure per square inch, in tons.	Time.	Mercury.	Copper.	Sp. grav.
1.	¾	12 hours	100	20·3	
2.	¾	12 hours	„	17·28	
3.	1	36 hours	„	20·5	
4.	1¼	17 hours	„	18·95	
5.	2	12 hours	„	18·4	
6.	gradually increased up to 1 ton	3½ months	„	39·02	12·76
7.	„	13 days, with intervals amounting to 54 days	„	38·43	12·56
8.	9	a few minutes	„	25·84	12·92
9.	15	„	„	28·57	
10.	18	„	„	28·4	13·01
11.	20	„	„	29·46	
12.	72	„	„	30·95	13·06
13.	72	„	„	32·82	12·93
14.	144	„	„	35·13	12·96
15.	144	„	„	34·87	12·57
16.	144	„	„	35·63	12·62
17.	20	30 minutes	„	33·04	
18.	36	30 minutes	„	30·25	12·88
19.	72	1 hour	„	32·34	
20.	30	2 hours	„	40·18	
21.	30	7 hours	„	44·34	12·38

On inspecting the above Table, it will appear that a moderate pressure continued for a short time leaves a binary compound of

the metals along with the quantity of mercury which may be supposed to be entangled among the crystals. When the pressure was very great, or was continued for a long time, the resulting amalgam invariably contained more than one equivalent of copper. I believe that this arises from a decomposition of the binary amalgam by the violent mechanical means adopted.

On the supposition that the copper retains its own specific gravity, the density of the above amalgams gives for the mercury a specific gravity of 14·985.

The *Amalgam of Silver* was generally produced by treating mercury with nitrate of silver. The action goes on until a hard mass of shining crystals is formed, consisting of about an equivalent of silver to one of mercury.

No.	Mercury.	Silver.	Sp. grav.	Remarks.
1.	100	52·6	14·68	From cold solution of nitrate of silver.
2.	„	100·3	....	Ditto ditto.
3.	„	115·4	....	Ditto ditto.
4.	„	115·2	13·25	Ditto ditto.
5.	„	155·8	12·34	Boiled in solution of nitrate of silver.
6.	„	106·4	12·49	From a hot concentrated solution of nitrate of silver.
7.	„	293·3	12·54	Button of amalgam formed by the electrolytic action of one cell of Daniell's battery.
8.	„	2614·0	11·42	Crystals formed on the edges of the above button of amalgam.

From the above Table, it appears that the amalgam most readily formed by the action of nitrate of silver on mercury is a binary compound: for the average result gives the proportion of 107·6 silver to 100 mercury. It will be noticed that the specific gravity of the specimens indicates, as in the case of the amalgam of copper, a very considerable contraction of volume, principally referable no doubt to the assumption of the solid state by the mercury, the specific gravity of which comes out 16·5 from the above and succeeding experiments on the amalgam of silver.

In the next Table, I give the composition of amalgams of silver after compression. Before placing it in the press, each specimen was mixed up with excess of mercury so as to form a thick paste. I should mention here, that, on making the analysis, it was found necessary to employ a temperature nearly sufficient to fuse the silver in order to drive from it the last portions of mercury.

No.	Pressure.	Mercury.	Silver.	Sp. grav.
1.	2½ tons for 1 day	100	33·78	
2.	3 tons for 3 days	„	37·76	
3.	72 tons for 1 hour	„	40·13	13·61
4.	72 tons for 1½ hour	„	40	13·78
5.	72 tons for 1½ hour	„	51·55	13·44
6.	72 tons for 20′	„	43·15	

The mean composition of the amalgam, after being pressed with 72 tons on the inch, was therefore 43·71 silver to 100 mercury. Allowing for mercury remaining among the crystals in an uncombined state, we may conclude that the solid amalgam containing the largest quantity of mercury is composed of one equivalent of silver to two of mercury.

Amalgam of Platinum.—To obtain this amalgam, platinum was deposited on mercury by the electrolytic action of two or three voltaic cells on the bichloride.

No.	Mercury.	Platinum.	Sp. grav.	Remarks.
1.	100	15·48	14·29	Metallic lustre when rubbed.
2.	„	21·6	....	Solid. Dark grey colour.
3.	„	34·76	14·60	Dark grey; no metallic lustre.

An amalgam of 12 platinum to 100 mercury possesses a bright metallic lustre, and is soft and greasy to the touch. Pressed with a force of 72 tons to the square inch, a hard button of dark grey amalgam is left, consisting of 43·2 parts of platinum to 100 of mercury. I infer therefore that the solid amalgam of platinum, which contains the largest quantity of mercury, is composed of two equivalents of mercury to one of platinum.*

The specific gravity of this amalgam appears to be nearly that which it would be on the supposition that no condensation of volume takes place on the union of the metals; but the specimens were too small to admit of very accurate determinations of specific gravity.

Amalgam of Zinc was obtained electrolytically from sulphate of

* Amalgam of platinum in the form of a thick paste may be obtained by exposing mercury to the action of bichloride of platinum for a sufficient length of time.

zinc; after some time the mercury lost its fluidity, and branching crystals began to be formed.

No.	Mercury.	Zinc.	Sp. grav.	Remarks.
1.	100	39·4	11·34	White and crystalline.
2.	„	122·8	8·935	Ditto ditto.
3.	„	184·9	8·349	Prepared from hot sulphate of zinc.

The first of the above three specimens, consisting of an equivalent of each metal, appears to be the amalgam which, containing the largest quantity of mercury, is yet solid. The specific gravity indicates a certain contraction of volume, but not nearly as much as that in the amalgams of silver and copper, but such as would place the specific gravity of the mercury at 14·1. Pressure seemed to have the effect of decomposing this amalgam, or at least of expelling mercury, until the amalgam consisted of about one equivalent of mercury to three of zinc.

No.	Pressure.	Mercury.	Zinc.
1.	¾ ton for 1 day	100	59·25
2.	1¼ ton for 1 day	„	69
3.	50 tons for 1 hour	„	76·7
4.	ditto	„	79·6
5.	ditto	„	75·9

Amalgam of Lead.—On making mercury negative in acetate of lead, a crystalline amalgam was gradually formed. The operation was stopped when the characteristic flat blue crystals of lead began to make their appearance. The amalgam was found to have a specific gravity of 12·64 (indicating 13·85 for its mercury), and to consist of 100 mercury to 69·83 lead, and, allowing for unavoidable excess of mercury, may be considered as a binary compound.

To ascertain the effect of pressure, a liquid amalgam was formed by heating the two metals together. It was then compressed with a force of three tons to the square inch for a day. A greater pressure than this would have caused the amalgam as well as the mercury to escape from the press. The result was a mass of bright crystals, easily fractured, which had a specific gravity of 12·11, and was composed of 100 mercury to 194 lead. I think

there can be no doubt that the pressure had partly decomposed the binary compound. It appears that little or no contraction of volume is occasioned by the combination of the metals.

Amalgam of Tin was obtained by making mercury negative in a solution of chloride of tin.

No.	Mercury.	Tin.	Sp. grav.	Remarks.
1.	100	51·01	10·518	Beautiful crystalline amalgam.
2.	„	44·12	10·94	Ditto ditto.
3.	„	70·7	....	Some unamalgamated tin crystals at the extremities of the amalgam.

The amalgam formed by the electrolytic process appears, therefore, to be a binary compound. Its specific gravity, along with that given in the next Table, shows a specific gravity of 14·1 for the mercury in combination. Pressure of the amalgam gave the following results:—

No.	Pressure.	Mercury.	Tin.	Sp. gr.	Remarks.
1.	1440 lbs. for 10′	100	75·9		
2.	1440 lbs. for 2 days	„	255·5		
3.	2724 lbs. for 2 days	„	392·4		
4.	5400 lbs. during 30 days	„	384·1	8·144	Pressure gradually increased.
5.	50 tons for 15′	„	402·3		
6.	2700 lbs. during 30 days	„	408·9		Pressure of 50 tons during 1 day did not afterwards drive out more mercury.

The above results show most decisively that pressure is able to decompose the amalgam of tin, the mercury left after long-continued high pressure having a volume little more than one-eighth of the entire mass.

I made an unsuccessful attempt to amalgamate hydrogen, by developing it at a low temperature (4° Fahr.) on mercury. It did not appear that the smallest quantity of hydrogen was taken up. This appears, however, to be an experiment worth repeating. I think it highly probable that, by using intense cold and very great pressure, an amalgam of hydrogen might be formed.

As metals generally retain their specific gravities when they meet to form alloys, it may be inferred that the foregoing experiments indicate the specific gravity of mercury in the solid state. This value, from the average of the thirty-six determinations of specific gravity above given, is 15·19.

XLVI.—*On the Occurrence of Titanium in Pig-iron, and some Remarks on the use of Titaniferous Minerals in the Manufacture of Iron and Steel.*

By Edward Riley, F.C.S.

[Read at the Newcastle Meeting of the British Association.]

The presence of small cubical red crystals, with a metallic lustre, has long been observed in the hearths of old blast-furnaces—they may be said, in fact, to be universally present to a greater or less extent—occurring most largely in the hearths of furnaces where clay ironstone, or silicious iron ores (such as the red hematite and Forest of Dean ores) are used. The crystals are always more abundant when the furnaces are used for making the best grey iron, the most perfect crystals that have come under my observation being some from the Low Moor ironworks; while the largest quantity were from the ironworks in the Forest of Dean, and the Pontypool ironworks, some of which crystals were massed together, and had the appearance of copper. The iron from the above works has a great commercial reputation for its quality, and as a rule, the better the quality of iron made in a blast-furnace, the greater is the quantity of titanium found in the hearths.

The examination of a large number of the hearths of the Welsh blast-furnaces, where common iron for rails and bars is chiefly made—in one works eighteen were inspected during their removal—the crystals were observed disseminated through the mass, but were only very small in size and minute in quantity.

The red crystals were first supposed by Wollaston to be titanium; but Wöhler subsequently showed them to be a mixture of nitride and cyanide of titanium, containing 18 per cent. of nitrogen and 4 per cent. of carbon. The composition of the crystals, however, varies—as some will be found to be readily converted into titanic acid on boiling with strong nitric acid, whereas others are quite unattacked by this re-agent.

Until recently the source of these crystals had not been very

clearly accounted for, as in all analyses of materials used in the blast-furnace, titanic acid or the oxide of titanium was very rarely if ever mentioned. Titanic acid has hitherto been considered an oxide occurring only in minute quantity, or found in minerals that are not largely disseminated—such as in Rutile and Anatase, in the pure or nearly pure state, in Iserine, Ilmenite, and numerous other minerals mostly mixed with a large percentage of iron. The following are two analyses of some Norwegian ore that has been used in the blast-furnace, and will be subsequently referred to:—

	1.	2.
Magnetic oxide of iron	46·14*	54·72
Titanic acid	36·88	40·80
Silica	13·32	1·58
Magnesia	2·07	2·13
Lime	·78	·66
Bisulphide of iron (iron pyrites) ..	1·05	—
	100·24	99·89
Metallic iron	33·39	39·62

No phosphoric acid was detected.

An experience of eleven years, in the almost exclusive examination of ores and products from iron works, has proved to me that titanium ought no longer to be considered one of the rarer elements, as it occurs very generally disseminated, and is a universal constituent of all clays, as was pointed out by me in a paper read before the Chemical Society last year, whence it seems that in furnaces where clay ironstone is used, the source of the titanium is the clay in the ore and the shale attached to it. In silicious ores, such as the hematites, the titanium is most probably obtained from Rutile, which is frequently found in quartz, and perhaps partly from the fire-bricks, and from the shale which is frequently used.

The minerals of titanium, viz., Rutile, and Titanic acid mixed with iron, are largely found in Norway, and can be brought over to this country at a very cheap rate. Rutile, which, commercially speaking, is pure titanic acid, can be purchased here for 10*l.* per ton, or even less if it were taken in large quantity; and iron ores, such as shown in the analyses given, can be bought at from 20*s.* to 40*s.* per ton.

Recently a series of patents has been secured by Mr. R. Mushet, for the use and application of titanium in the manufacture of iron and steel, and for alloying titanium with iron and

* These analyses were made in my laboratory by my late pupil, Mr. Betley.

steel, in which very beneficial results are claimed for the action of the titanium.

Before entering upon the question as to the effects of titanium, it will be well to consider if titanium alloys with iron, and, if so, to what extent. Up to the end of 1862 I had examined many samples of pig-iron, and Mr. Mushet's steel itself specially, with the view of detecting titanium; but in no case could I obtain any distinct evidence of its presence, except occasionally as a minute trace. My conclusion at that time was that titanium did not alloy with iron, and my opinion on this point was strengthened by the results of M. St. Claire Deville, of Paris, who has paid especial attention to the subject; Dr. Percy has also observed that he could never find it. M. Deville mentioned to me, in the course of some conversation on the subject, that he had occasionally seen red crystals of titanium in the pig itself, and it was only then that he could detect the presence of the metal. The general opinion of English chemists, who had paid attention to the subject, was that titanium did not practically alloy with iron.

At the end of last year some samples of pig-iron were submitted to me, one of which was made from red hematite mixed with $7\frac{1}{2}$ per cent. of Norwegian ore, similar to that of which the analyses have just been given. The analysis of this sample of pig gave distinct evidence of the presence of an appreciable amount of titanium; and in other samples, sent at the same time, reported to be made from red hematite alone, to my surprise titanium was also found, but not quite to such a large amount. This could not be satisfactorily accounted for until the persons sending me the pig, informed me that 10 per cent. of Irish (Belfast) ore had been mixed with the hematite; and on examining this ore, it was found to contain some amount of titanium, as seen by the following analysis:—

BELFAST IRON ORE, dried at 280° Fahrenheit.

Silica	9·87
Peroxide of iron	27·93
Protoxide of iron	5·08
Alumina	34·57
Titanic acid	3·51
Manganese	traces
Lime	·91
Magnesia	·62
Combined water	19·36
Phosphoric acid and copper	traces
	101·85
Metallic iron %	23·5

The use of this ore in the furnace was attended with considerable advantage, on account of its high percentage of alumina, thus forming a more readily fusible double silicate with the silica contained in the hematite.

The method pursued to detect titanium was the same as that adopted and given in my paper in the Journal of the Chemical Society for 1862, page 311. It however required no very special method to point out its presence, and it was readily found in the silica obtained in the portion of pig used for the determination of phosphoric acid, by simply treating the silica with hydrofluoric and sulphuric acids, evaporating to dryness and igniting. Thus 120·845 grns. of pig gave silica 4·29, which left a residue, when treated as above, of 0·31. This was slightly tinged in colour by iron, and on fusing it with bisulphate of potash, dissolving the fused mass in cold water, and boiling, the characteristic precipitate of titanic acid was obtained, which gave the reactions peculiar to titanic acid in the blowpipe flame with microcosmic salt. The whole of the titanic acid cannot be separated with the silica, and a considerable amount is in solution with the iron.* However, to

* The following are methods which have been adopted to separate the titanic acid :—A weighed portion of the borings of the pig are treated with fuming nitric acid in a flask, a few drops of hydrochloric acid added from time to time, the whole being well boiled. The contents of the flask are then transferred into a porcelain dish, evaporated to dryness and heated strongly. On cooling, it will be found that oxide of iron readily detaches itself from the dish, and can be easily transferred into a beaker, the portions left on the dish being dissolved in hydrochloric acid, and poured on the contents of the beaker; the dish may be washed, or nearly so, with strong hydrochloric acid. The contents of the beaker are boiled for two or three hours until complete solution of the iron is effected; and as some quantity of hydrochloric acid is required for this, my usual plan is to allow a large portion of the excess of acid to evaporate in the beaker, retaining only as much as is requisite to keep the iron in solution. The silica is filtered off in the usual way, after diluting with water and adding a few drops of hydrochloric acid on the filter to dissolve the basic salt formed by the water. By this means the silica can be obtained very nearly white after burning off the graphite, and very little iron will be found with it, unless the pig contains much phosphorus, as the silica invariably contains more or less phosphate of iron from insoluble phosphide of iron, which cannot be completely dissolved out by hydrochloric acid. In the filtrate from the silica the sulphur in the pig may be determined, and subsequently the phosphoric acid, by first removing the excess of chloride of barium used to precipitate the sulphuric acid. Before determining the titanium and phosphoric acid, the residue from the silica should be fused with bisulphate of potash, dissolved in water, and added to the solution of iron in which the phosphorus and titanium are to be determined. The solution is reduced with sulphite of soda, and the excess of sulphurous acid driven off by boiling. The solution is then nearly neutralised with ammonia, and acetate of ammonia or soda added; and if there is only a small quantity of phosphoric acid,

determine accurately titanic acid, oxide of iron ought to be entirely absent, as it either prevents its precipitation altogether, or materially retards it. This is in fact the great reason why titanic acid has been so frequently overlooked, and so many errors made.

Titanium may, however, be found more satisfactorily and more readily, during the process usually adopted to determine the amount of graphite in pig-iron, provided a large quantity of the pig be operated on. In the analysis of the pigs alluded to, about 200 grains of the pig were dissolved in dilute hydrochloric acid; when the pig was nearly all dissolved, and the action of the acid had ceased, more hydrochloric acid was added, and the solution well boiled, so as thoroughly to extract the iron. The solution was then thrown on dried counterpoised filters encircling each other, and the filter well washed to remove all the iron. It was then treated with dilute potash, and washed once; then re-treated with it, so as entirely to remove the silica. The potash

there will always be sufficient peroxide of iron to precipitate it, but if not, a few drops of nitric acid must be added, so that the precipitate produced is distinctly red, and the solution is boiled and filtered as quickly as possible. This precipitate may be at once treated, or if it contains much peroxide of iron in excess of that sufficient to form phosphate of iron, it is better to re-dissolve it in hydrochloric acid, re-reduce it with sulphite of soda, and repeat the operation above described. The precipitate is then dissolved in hydrochloric acid, and chloride of magnesium, ammonia, chloride of ammonium, and tartaric acid added, the precipitate produced being allowed to stand two nights; then the ammonia-phosphate of magnesia is filtered off, dried, ignited, and weighed, and the phosphoric acid calculated from the pyro-phosphate of magnesia. The filtrate from the phosphoric acid is treated with sulphide of ammonium, and the sulphide of iron separated, the filtrate evaporated to dryness, ignited, and burnt in a muffle; or evaporated nearly to dryness, transferred into a Florence oil-flask, and treated with fuming nitric acid until all the tartaric acid is destroyed; in either case the residue is fused with bisulphate of potash, or where nitric acid is used, this is driven off with sulphuric acid. The product of the fusion with bisulphate of potash is dissolved in cold water, boiled for some hours, and allowed to stand a night in a warm place, when the titanic acid is filtered off and washed with dilute sulphuric acid—dried, ignited, and weighed. If the determination of phosphoric acid is not required, then the precipitate produced (either by one treatment or two) by the alkaline acetate, may be dried (without washing), burnt, and fused with bisulphate of potash, and dissolved in cold water, when a little phosphate of iron, which remains insoluble, is separated; and the solution being boiled, the titanic acid is precipitated, and may be separated as before.

Neither of the above two processes is very satisfactory for the quantitative determination of titanic acid. The first is very tedious, and the destruction of the tartaric acid very troublesome; while in the second method, the phosphate of iron (insoluble in the bisulphate of potash) cannot be washed without passing through the filter; very frequently also the small amount of iron keeps up the titanic acid, as iron, even in small quantities, has a very great effect in preventing the precipitation of titanic acid, so that it is always advisable to add a little sulphite of soda, which reduces the oxide of iron and facilitates the precipitation of the titanic acid.

was thoroughly washed out, and the filter treated with hydrochloric acid, thoroughly washed, and dried at 250° Fahrenheit, until the weight was constant. This gave the graphite, on burning which, a residue of a dirty light brown colour was left, which, on being fused with bisulphate of potash and treated as before, proved to be nearly pure titanic acid, as will be seen from the results below :—

	Grains of Pig taken.	Graphite and Titanic Acid.	Residue after Burning.	Titanic Acid obtained.
No. 1 Pig ..	205·68	7·82	1·23	1·085
„ 2 „	207·05	7·85	·835	·745
„ 3 „	216·86	7·04	·33	·28

The amount of titanic acid, or rather residue, obtained from the silica after it had been volatilised with hydrofluoric and sulphuric acids, when the pig was dissolved in nitro-hydrochloric acid, evaporated to dryness, and re-dissolved in hydrochloric acid—is given below :—

	Grains of Pig taken.	Silica obtained.	Residue by Hydrofluoric and Sulphuric Acids.
No. 1	120·845	4·29	·31
„ 2	127·93	8·659	·20
„ 3	122·55	9·22	·265

This residue, chiefly titanic acid, contained, however, some iron, and was not so pure as that obtained by burning the graphite, given in the above table. The following are the tabulated results of the analyses of the three samples of pig :—

	1.	2.	3.
Carbon..	3·31	3·18	3·11
Silicium	1·86	3·28	3·55
Iron	93·47	92·79	92·04
Manganese	·50	·48	1·09
Sulphur	·071	·058	·112
Phosphorus	·076	·062	·093
Titanium	1·150	·71	·470
	100·437	100·560	100·465

In all these the carbon was combined; and traces of antimony, nickel, copper, and cobalt were found in all three samples.—Samples 1 and 2 were No. 3 grey iron; and sample 3 was bright iron.

The percentage of titanium given in the above analyses differs from that in the preceding table, probably in consequence of the hydrochloric acid dissolving some of the titanium. From 15 to 16 grns. of the pig are dissolved in nitro-hydrochloric acid, and the solution evaporated to dryness; the silica separated in the usual way and volatilised with hydrofluoric and sulphuric acids; the residue fused with a little bisulphate of potash, dissolved in cold water; and the liquid added to the filtrate from the silica. The solution is precipitated with acetate of soda or ammonia, first nearly neutralising it with ammonia; after boiling well, the basic peracetate of iron is filtered off, and well washed, adding occasionally a drop or two of the alkaline acetate. The filter is then dissolved in hydrochloric acid, and peroxide of iron precipitated by ammonia, filtered, dried, and ignited in the usual way. The peroxide of iron is then dissolved in hydrochloric acid, and the small amount of silica present separated; the solution is reduced with sulphite of soda; and the iron determined with a standard solution of bichromate of potash. This gives the percentage of iron, or of pure peroxide of iron; and the difference between the peroxide of iron weighed, and that determined by standard solution, is considered to be titanic acid and phosphoric acid. The phosphoric acid having been determined by another distinct operation, the amount present in the peroxide of iron is calculated and deducted from the above difference—the remainder being considered to be titanic acid, from which the percentage of titanium in the pig is calculated. This determination by loss is not so satisfactory as a direct determination, and is probably a little high; and the true percentage of titanium will probably lie between that given in the table and that in the analyses. Subsequently to the analyses of the above three samples of pig, a sample of iron made wholly with hematite was tested for titanium, but none was detected. Recently I have examined some samples of pig-iron made from a mixture of Cornish ores, Irish bog-ore, and hematite ore; the result shows that the pig contains some amount of titanium; the following is a partial analysis* of the Cornish ores used:—

Silicious matter	23·38	21·70	27·18	21·03
Peroxide of iron	41·96	56·32	47·32	70·20
Peroxide of manganese	25·77	16·11	16·25	2·45
Percentage of metallic iron ..	29·38	39·43	33·14	49·14
„ „ manganese ..	16·08	10·25	10·34	1·55

These ores contained a little phosphoric acid.

* Analysis made in my laboratory by Mr. Betley.

The following are the results of the analyses of three samples of this pig, the titanium being determined as in the other analyses of pig given :—

	I.	II.	III.
Graphite	3·12	3·010	2·615
Combined carbon..	·310	1·020	·074
Silicium	2·590	2·550	3·325
Iron	87·900	86·880	84·256
Manganese	5·850	6·370	8·087
Nickel and cobalt..	·060	·110	—
Copper with a little antimony ..	·060	·045	·064
Phosphorus	·147	·154	·201
Sulphur	·026	·026	·017
Titanium	·790	1·150	1·629
	100·853	101·315	100·268

Samples I and II were made with a mixture of ½ Cornish ore; ½ Irish bog-ore, ½ hematite; and sample III, ⅛ Irish bog-ore, ⅞ Cornish ore. The Irish bog-ore contained 7 to 9 % of manganese.

These samples of pig were Nos. 1 and 2, with here and there patches of bright iron. Nos. 1 and 2 were drilled, but were rather hard; No. 3 was too hard to drill, or could only be drilled with great difficulty. They were made specially to see to what extent, on a large scale, manganese could be made to alloy with iron; and also if a pig could not be made in this country similar to *Spiegeleisen*, and adapted for the purpose of carbonising the iron after blowing by the Bessemer process. The percentage of manganese in the analysis of sample III is the highest that has ever come under my notice in grey pig-iron.

The question now arises — In what state does the titanium exist in the pig—is it, or is it not, alloyed with it? The pig itself has been carefully examined with the microscope to see if any red nitride crystals could be discovered, but no indications of them have been seen. The residue, after dissolving the pig in hydrochloric acid, washing out all soluble matter, and drying, has also been examined, but only distinct graphite plates could be seen, with transparent gelatinous silica, having the appearance of chalcedony; and also some of this residue, after the silica had been separated, was examined, but no indication of any other substance besides the graphite could be seen. From the above it is evident that the titanium must be either disseminated through the pig in a finely divided amorphous condition, or it must be alloyed with it.

Samples of Mr. Mushet's steel, in the manufacture of which titaniferous ores had been used, were also examined, but in no

case was any evidence of the presence of titanium afforded. Several experiments conducted on a small scale with titaniferous iron ores show that no increase in the yield of iron is obtained by the presence of titanic acid, and that when this substance is present in any quantity it is very difficult to flux, or to get a good cinder; so that it is always necessary to have a large amount of an easily fusible silicate, before satisfactory results can be obtained in the reduction of ores containing titanic acid. The following are the results of the dry assays of some titaniferous iron ore, containing by wet assay 39·08 per cent. of iron :—

	1.		2.	
Iron ore	500	500	500	500
Clay	100	100	50	100
Lime	250	230	150	180
Anthracite	80	75	75	70
	930	905	775	850

The two assays marked 1 were perfect, and a good button of iron obtained, yielding 37·76 per cent. of iron in the ore, the cinder being of a dark blue colour; but in the assays marked 2, the cinder was almost black, semi-fused, and contained cavities with acicular crystals.

It must, however, be admitted, that when titanic acid is present in iron ores, it appears to impart a steely nature to the iron reduced from them, somewhat similar to that obtained by the use of manganese; and fluxes that have been used with advantage at Sheffield have, on analysis, been proved to contain a high percentage of titanic acid. The pig-iron made with 7½ per cent. of titaniferous iron ore, of which the analysis is given, proved also to be an iron of very great strength, and excellent quality both for castings and for the Bessemer process.

In conclusion, my opinion as to the use of titanium is, that it appears to have some beneficial effect in the manufacture of iron and steel, and to act somewhat similarly to manganese. The rationale of its action possibly is that the titanium acts as a carrier of cyanogen to the steel, from its known affinity for carbon and nitrogen. The action of manganese is, however, by no means well understood; the same may be said of the cyanides; and to determine it requires the experiments to be more carefully conducted than has been hitherto done, before we can solve the question as to the part (if any) that nitrogen plays in the manu-

facture of steel. The above points are at the present time engaging my attention; but my object in this paper is to prove that under certain conditions titanium is a constituent part of pig-iron, and not to enter into theoretical considerations on the composition of iron and steel.

XLVII.—*On the Detection of Nitric Acid.*

By Hermann Sprengel, Ph.D.

Reactions for the detection of nitric acid may be divided into two principal groups, the first embracing those in which the presence of the acid is inferred from the production of some oxidation; the second, those which consist in the formation of new compounds, containing not only some of the oxygen, but also the nitrogen originally existing in the nitric acid. From the circumstance that many bodies act as oxygenants under the same conditions as nitric acid, the mere evidence of oxidation during the search for the acid cannot be taken as a satisfactory proof of its presence.

When the nitrate is in a greatly diluted state, or in the presence of comparatively large quantities of organic matter, resort must be had to Higgin and Price's iodine starch reaction, but in all other cases, the reactions of the second group are decidedly preferable, because they leave no doubt about the presence or absence of the higher oxides of nitrogen.

Richmont's well-known coloration of sulphate of iron by binoxide of nitrogen has, until now, always been regarded as the reaction, *par excellence;* but it will be seen that the one I am going to describe, surpasses it both in delicacy and rapidity.

It has long been known that nitric acid has a most energetic action upon phenyl-compounds, accompanied, in a great many cases, with the production of a remarkable intensity of colour, which, so far as I know, has not yet been applied to the mutual recognition of these bodies.

The manner in which I proceed is as follows:—I make a solution of 1 part of phenol in 4 parts of concentrated sulphuric acid, and then dilute it with 2 parts of water. If the substance to be

examined for nitric acid is in solution, I evaporate it in a porcelain crucible or its cover, and let fall one or two drops of my phenyl-sulphuric acid upon the residue, at a temperature of about 100° C. By the excess of the sulphuric acid, any nitrates, if present, will be decomposed, and the nitric acid derived from them will directly form nitro-compounds with the phenol, which are indicated by the production of a reddish-brown colour. When neither organic matters, nor compounds of chlorine, iodine, and bromine, from which sulphuric acid easily separates carbon or the haloïds, are present, this coloration is in itself convincing. But for fear of their presence, it is better, in all cases, to add a drop or two of strong ammonia to the coloured product, when the haloïds will be dissolved in the form of colourless salts, and the carbon remain suspended in small particles, not interfering with the recognition of the characteristic yellow solution of the nitrophenylate of ammonia. I have to remark, that frequently, after the addition of ammonia, I have noticed, instead of a yellow, the appearance of an unstable emerald green colour, which changes into rose after the addition of an acid, and occasionally a greenish yellow, in all different shades, which doubtless have their origin in the formation of two different bodies, either a green and yellow one, or a blue and yellow one, from the mixture of which the green would result. But as most eyes can recognise yellow as well as green, I have not hitherto undertaken the examination of this colour more minutely. Laurent has already noticed a similar phenomenon in treating dinitrophenylic acid with nascent hydrogen, but has given no further explanation. It very likely depends upon the relative proportions, in which mono-, di-, and trinitrophenylic acids are formed. Hereafter I hope to investigate this subject further. For the present it may suffice to say that we have here the means of detecting nitric acid with speed and accuracy in extraordinarily small quantities. I have been able to recognise it in the residue of a minute drop of water, which did not contain more than 0·000006 grn. of nitric acid, while four of these drops were not sufficient to show the slightest effect by Richmont's test. I lately had to examine several specimens of well-water, where one single drop was more than sufficient to show clearly the presence of nitric acid, when tested by the above-described process. I need scarcely say that in order to conduct these experiments satisfactorily, it is very necessary to bear in mind the old rule of working in as concentrated a style as possible. I myself

prefer to evaporate the matter drop by drop, taking care that each drop falls on the same spot, and then adding to the residue as small a quantity of the reagents as will afford the requisite test.

Phenyl compounds appear to me particularly fitted to take a prominent part in the detection of nitric acid. Some time since Dr. Hofmann told us of a phenyl-base, *chrysaniline*, the insolubility of whose nitrate may possibly furnish a process for the estimation of nitric acid.

St. Bartholomew's Hospital,
Oct. 27th.

XLVIII.—*On the Igniting Point of Coal-Gas.*

By Dr. E. Frankland, F.R.S.

[From the Journal of Gas-lighting.]

The temperature at which coal-gas will ignite under ordinary, or extraordinary conditions, is a circumstance of considerable importance, both to manufacturers and consumers of gas; nevertheless the difference of opinion which evidently prevails, even amongst those who are intimately acquainted with the properties of coal-gas, proves that the subject has not hitherto received that attention which it obviously merits. Under these circumstances, the following experiments, and the conclusions drawn from them, although they are far from exhausting the subject, may not perhaps be altogether unacceptable as a contribution to this part of the history of coal-gas.

The heterogeneous mixture of gases and vapours, known as coal-gas, may, for our present purpose, be assumed to consist of:—

Olefiant gas and other luminiferous hydrocarbons,
Light carburetted hydrogen, or fire-damp.
Hydrogen.
Carbonic oxide.
Bisulphide of carbon.

Now, as these constituents can, to some extent, become separated from each other, under certain circumstances, it is desirable,

at the outset of the inquiry, to examine separately their respective igniting points.

1. Olefiant gas, which may be taken also as a type of the remaining luminiferous hydrocarbons, could not be inflamed by a hot iron, unless the latter were heated until it appeared of a cherry-red colour in the daylight of a tolerably well-lighted room.

2. The igniting point of light carburetted hydrogen was carefully determined by Davy, to whose observations I have not a word to add. He says that, "light carburetted hydrogen can be inflamed by *white hot sparkling iron*, but not by iron at a red heat; it is, therefore, much less inflammable than hydrogen or carbonic oxide, and less so than olefiant gas." Bischof says that it cannot be inflamed by burning tinder, even though the tinder be strongly blown upon.

3. Hydrogen inflamed at a lower temperature than olefiant gas, but it could not be ignited by a rod of iron, unless the latter were heated to a temperature considerably beyond visible redness in a tolerably well-lighted room.

4. Carbonic oxide inflamed at a temperature somewhat greater than that at which hydrogen ignited, but lower than that necessary for the inflammation of olefiant gas.

5. Bisulphide of carbon vapour ignited at 300° Fahr.

In some experiments made in connection with the gas explosion in Wood Street, I had occasion to observe that when coal-gas is allowed to mix with air contained in a space, partly inclosed, but still communicating freely with the atmosphere, such as a large gas-main open at one end, there occurred an approximate separation of the lighter from the heavier constituents of the gas; thus, samples of the explosive mixture taken from such a space were found on analysis to contain olefiant gas, luminiferous hydrocarbons, carbonic oxide, and bisulphide of carbon, with but a small percentage of light carburetted hydrogen, and mere traces of hydrogen, although the two latter gases constitute, as is well known, the chief bulk of coal-gas. These gases must, therefore, have rapidly made their way out of the partially-inclosed space into the atmosphere. This behaviour of the different constituents of coal-gas, when the latter is slowly admitted into one end of an open main containing atmospheric air may not inaptly be compared to that of a number of birds, of different powers of flight, entering at one end of the pipe, and making the best of their way towards the opposite extremity. At every moment after the

entrance of the birds, the percentage of those of swift flight would diminish near the entrance-end of the pipe, whilst that of the birds of slower velocity would obviously increase in the same ratio.

Graham has proved that the rapidity with which gases diffuse into each other, or into a vacuum, is inversely proportional to the square roots of their specific gravities; and, although there are some circumstances in the case of the open gas-main, or partially-enclosed space, which would somewhat interfere with this ratio, yet, for all practical purposes, Graham's law may be assumed to express correctly the different velocities with which the constituents of coal-gas would hasten to escape from the space in question.

These velocities of diffusion are as follow:—

Bisulphide of carbon	1
Olefiant gas	1·66
Carbonic oxide	1·66
Light carburetted hydrogen . . .	2·19
Hydrogen	6·23

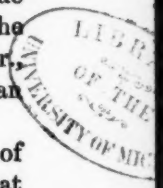
All other luminiferous hydrocarbons existing in coal-gas must have a diffusion velocity lower than that of olefiant gas.

Thus the effect of diffusion of coal-gas in an open horizontal pipe, or other similar partially-inclosed space, would be to form an explosive mixture, containing chiefly hydrogen as the combustible gas, at or near the open extremity of the pipe; whilst the explosive mixture formed near the end of the pipe where the gas entered, would contain chiefly carbonic oxide, olefiant gas, and bisulphide of carbon.

It is obvious, from experiment No. 3, that the explosive mixture, formed near the mouth of the tube, would ignite at a somewhat lower temperature than that required for the ignition of an explosive mixture containing all the constituents of coal-gas. Still, even this more inflammable mixture could not be ignited below a red heat distinctly visible in the daylight of a room. It might, however, be expected that the explosive mixture formed at the opposite extremity of the tube, would be capable of ignition at a still lower temperature, owing to the continued increase in the proportion of the highly inflammable but sluggish bisulphide of carbon, which could, doubtless, under favourable circumstances, increase to at least ten times the amount originally contained in

the coal-gas. In order to ascertain the effect of the presence of a considerable percentage of bisulphide of carbon vapour upon the inflammability of the constituents of coal-gas, and especially of carbonic oxide and olefiant gas, the following experiments were made :—

6. Carbonic oxide was mixed with about 3 per cent. of the vapour of bisulphide of carbon, and was then allowed to issue from a jet into the air. The jet of gas readily ignited on the approach of a glass tube containing oil heated to 410° Fahr., the igniting point of the gas being probably not higher than 350° Fahr.



7. Hydrogen containing the same amount of bisulphide of carbon vapour, ignited by contact with a tube containing oil at 420° Fahr.

Here, then, was a phenomenon which would seem to indicate the alarming possibility of the ignition, at a comparatively very moderate heat, of explosive mixtures of coal-gas and air; fortunately, the next experiments entire allay any apprehensions on this score.

8. Olefiant gas, impregnated with 3 per cent. of the vapour of bisulphide of carbon, did not inflame at a perceptibly lower temperature than when free from the admixture of the sulphur compound.

9. To the highly-inflammable mixture of carbonic oxide and vapour of bisulphide of carbon, used in experiment No. 6, a minute trace (not 0·1 per cent.) of olefiant gas was added; instantly, the igniting point of the mixture was raised to that of pure carbonic oxide.

10. A similar experiment with the hydrogen mixture (No. 7) gave a corresponding result.

Thus, the extraordinary inflammability which is imparted to carbonic oxide and hydrogen by the vapour of bisulphide of carbon, is entirely removed by mere traces of olefiant gas; and it is probable that the other luminiferous hydrocarbons contained in coal-gas would produce the same effect. In order to complete this part of the inquiry, it now only remained to extend these experiments to coal-gas itself.

11. Coal-gas could not, even under the most favourable circumstances induced by diffusion, be ignited at a temperature perceptibly below that described in experiment No. 4, as necessary for the inflammation of carbonic oxide.

12. When coal-gas was mixed with 3 per cent. of bisulphide of carbon vapour, its igniting point was not lowered in the slightest degree.

Having thus proved that any amount of diffusion can have but a very slight effect upon the inflammability of explosive mixtures of coal-gas and air, the following experiments were made, to decide the disputed point, whether coal-gas can be inflamed by sparks:—

13. Hydrogen was readily inflamed by sparks struck from flint and steel.

14. Carbonic oxide was also readily ignited in a similar way.

15. The mixture of coal-gas and air, issuing from a wire-gauze burner, was repeatedly, and easily, inflamed by the sparks struck from flint and steel.*

These results are quite in conformity with the experience of gas-engineers and managers, several letters from whom are now before me, describing the ignition of gas from the sparks elicited by the contact of a workman's pickaxe with stones, the chipping of a main, &c. The notion that coal-gas will not inflame under these circumstance has, doubtless, arisen from the impossibility of so igniting the gas of coal-mines; but the combustible gas existing in British coal-mines has been proved, by very numerous analyses to be light carburetted hydrogen only—no trace of hydrogen, carbonic oxide, or olefiant gas being ever present in it. Now, the igniting point of light carburetted hydrogen, as already explained, is very much higher than that of the other combustible gases present in coal-gas; and hence, whilst the mine may be safely lighted by the "steel mill," the use of such an instrument in an explosive mixture of coal-gas would infallibly cause ignition. A word of warning as to the use of the safety-lamp in gas-works may perhaps not be here out of place. Even in the difficultly inflammable fire-damp mixture of coal-mines, the Davy lamp was known, by its inventor, to be unsafe under certain conditions,—as when placed in a strong draught or rapidly swung to and fro. Any degree of insecurity thus attaching to the safety-lamp in mines is increased tenfold when it is used in explosive mixtures of coal-gas; and hence it is highly desirable that the gauze of such

* These experiments were made with the *coal-gas* supplied to St. Bartholomew's Hospital, but the author has since found that *cannel-gas* is less easily inflamed. The cannel-gas supplied to the Royal Institution could not be thus ignited by sparks from flint and steel.

lamps should be finer than that used in the miner's lamp, and also that the workmen should be stringently prohibited from placing the lamps in a draught of explosive gas, or swinging them to and fro, since the neglect of these precautions may easily cause disastrous explosions.

In conclusion, the results arrived at may be thus shortly summed up:—

1. Coal-gas cannot, even under the most favourable circumstances, be inflamed at a temperature below that necessary to render iron very perceptibly red-hot by daylight in a well-lighted room. But this temperature is considerably below a red heat visible in the open air on a dull day.

2. This high igniting point of coal-gas, under all circumstances, is due in a great measure to the presence of olefiant gas and luminiferous hydrocarbons.

3. The igniting point of explosive mixtures of the gas of coal-mines is far higher than that of similar mixtures of coal-gas; consequently, degrees of heat, which are perfectly safe in coal-mines, may ignite coal-gas; hence, also, the safety-lamp is much less safe in mixtures of coal-gas than in those of fire-damp.

4. Explosive mixtures of coal-gas and air may be inflamed by sparks struck from metal or stone. Thus an explosion may arise from the blow of the tool of a workman against iron or stone, from the tramp of a horse upon pavement, &c.

5. Explosive mixtures of coal-gas may also be ignited by a body of a comparatively low temperature, through the medium of a second body, whose igniting point is lower than that of coal-gas. Thus sulphur, or substances containing sulphur, may be inflamed far below visible redness; and the contact of iron below a red heat with very inflammable substances, such as cotton-waste, may give rise to flame, which will then, of course, ignite the gaseous mixture.

XLIX.—*On the Manner in which Cotton Unites with Colouring Matter.*

By Walter Crum, F.R.S.

THIRD MEMOIR.

After my last communication to the Chemical Society, printed in the January number of this Journal, I intended to do little more on the subject of this paper than to complete the few drawings which were then projected. But being deprived of the assistance in delineating on which I had at first depended, and driven to have the objects drawn under my own eye, it soon appeared that further inquiry would render the investigation much more complete. By then applying myself more seriously than I had before done to microscopic observation, and by taking advantage of the instructions and assistance kindly afforded me by Mr. Hennedy, of Glasgow, in the slicing of transverse sections, together with the valuable co-operation of my assistant, Mr. Walter M'Farlane, in the preparation of materials and dyes, I have been enabled to ascertain the additional facts, and to prepare the drawings, which I now beg to present to the Society.

I shall describe dried cotton, and its behaviour with mordants, in four different stages of its growth :—

1. Ripe cotton.
2. A cotton which I shall call three-fourths ripe.
3. A half-ripe cotton.
4. The youngest cotton found in commerce.

MATURE COTTON.

Plate I gives a side view of various forms of cotton fibre in a state of maturity, mounted dry, and magnified about 400 diameters. The shadows are deeper, of course, than when the objects are mounted in fluids, but the inequalities of the surface are also better shown. At No. 2, Plate III., are transverse sections of the same fibre mounted dry; and at No. 1 they appear as mounted in glycerin jelly. It will be observed that few of them have the

complete cylindrical form. I have examined specimens of wool used for spinning, in which that form is scarcely to be found, except at the smaller end. It will be seen, also, from these drawings, that the cotton fibre is not a hollow tube or bag filled with air, and more or less collapsed, as it has hitherto been represented to be, but that in proportion as it is rounded, it has become filled up with apparently solid matter (like the liber fibre of flax), sometimes altogether, and at other times leaving clear passages through the centre.

UNRIPE COTTON.

The youngest or least ripe of the fibres of cotton, as it is imported, are those of the small glazed tuft, found among the rejected portions of cotton wool in its preparation for spinning. They are identical with the white specks I have already often referred to, which occur upon dyed fabrics, and to which the name of *dead cotton* has been given. Plate II. contains specimens of these fibres viewed lengthways and mounted dry. In glycerin jelly they appear still more transparent, and in Canada balsam they are scarcely distinguishable from the surrounding medium. At No. 8, Plate III., are transeverse sections of the youngest fibres mounted in glycerin jelly. They are so thin that they can only be made to stand upright where the section is bent. In many of them the sides adhere to each other so firmly that no line can be detected to mark a division between them, for even the rough treatment of the knife does not always serve to separate them. Others, however, have a slight mark between the two outlines, chiefly at the end of the section, and then they somewhat resemble the thinnest of the half-ripe fibre.

Plate II. contains also side views of the cotton which I propose to call *half ripe*, or in the second stage of maturity, mounted dry.

This is the wool contained in an Algerian pod, pulled green, and slightly open when dry, and I have found it the most interesting of the unripe cottons for the purposes of this inquiry. No. 4, Plate III., shows the microscopic appearance of transverse sections of this half-ripe cotton mounted in glycerin jelly. A line is always to be observed in the centre, pointing out that the flat blade consists of two walls, and that it is a flattened bag or tube.

I have found a distinctly marked *third stage*, which I have called *¾ths ripe*, in a pod of Orleans cotton of the same external appearance as the Algerian pod, containing the half-ripe wool. The

walls of this fibre are considerably and uniformly thickened, but the fibres themselves are comparatively flat, and none of them are cylindrical. It is represented in transverse section at No. 6, Plate III.

Commencing with the thin and fat blade (of dried cotton), whose section shews no apparent opening, the ripening of the fibre thus goes on, by the gradual thickening of its walls, until it assumes the more or less cylindrical and solid form of ripe cotton exhibited in Plate III., Nos. 1 and 2. On first observing that fact, there did appear to me, as well as to physiologists of greater experience who saw the objects, some authority for applying the generally understood principle of a formation of new and separate matter in the process of ripening; and accordingly, in pages 12 and 13 of this volume, I ventured such an explanation. It must now, however, as well as the inferences there drawn from it, be considered unsatisfactory, being without direct evidence, and contradicted—by analogy at least—in so far as it can now be shown that the substance of the thin wall, as it exists in the half-ripe fibre, and after being removed from the plant and dried, is itself capable of expansion, so as not only to give the fibre the cylindrical form, but to fill up a great part of the interior of the cylinder.*

Of the Half-ripe Cotton artificially expanded.—When the half-ripe but still perfectly flat and thin dried fibre (No. 4, Plate III.) is soaked in a solution of caustic soda of specific gravity 1·300 or 1·400, it at once assumes the round solid form of ripe cotton; differing from the naturally matured fibre only in being smaller, more generally cylindrical, and in having a larger aperture in the centre. It is represented at No. 5, Plate III.

To produce this change it is best to soak the unripe fibre in water before dipping it in the strong caustic soda, without which precaution it is apt to become matted together and less fit for subsequent operations. After the soda it is washed in water, then treated with a weak acid, and again washed.

It is well known that *mercerized* cotton, as the ordinary cotton

* The error pervades a great part of pages 12 and 13. It may, in some measure be corrected by substituting the words "*cotton in its expanded form*" where the expressions "*new deposit*" or "*secondary deposit*" occur.

With reference to other statements in pages 12 and 13, it will be observed that colourless openings are now readily seen in the coloured sections, and that new observations have been made on the effect of bleaching on the cotton fibre, and on the growth of cotton in the pod.

wool when so treated has been called, retains, after washing, none of the alkali that had swelled it. The increase of magnitude which the half-ripe fibre thus acquires is due, therefore, altogether to an expansion of the cell-wall, or a separation from each other of the inner and outer surfaces of that wall.

The youngest fibres do not seem to become rounded by caustic soda.

It may now appear not improbable that by the natural process of ripening an effect is produced similar in character to that which is given to the unripe fibre by artificial means, and that the natural expansion may be ascribed, not to the importation of a new kind of matter, coating the interior of the original cell-wall, but to a strengthening and rendering elastic of the membrane already existing of the wall itself, so as to produce the separation from each other of the cells or laminæ, or other structure of which it must consist.

The singular effect of strong alkaline solutions upon cotton-woven fabrics was discovered by Mr. John Mercer, and patented by him in 1850. From the transverse section of the mature fibre thus altered, as shown at No. 3, Plate III., it will be seen that the action of the soda completes the cylindrical form of that fibre, at the same time greatly enlarging its volume, and filling up almost entirely the central cavity. The twisting of the fibre is also much increased, as shown at B, Plate IV., and there is a consequent shortening of it, sufficient to account for the shrinking in length and breadth, and the thickening of any woven fabric which is made to undergo the mercerizing process. Diagonal lines are sometimes seen in these ripe mercerized fibres, giving the impression of a spiral structure; but they are evidently the creasing or corrugating effect of extreme twisting. Diagonal lines, apparently also from the effect of creasing, may occasionally be detected in the original flat unripe fibre, Plate II. They seem to cross each other where the two sides of the fibre can be viewed in the same focus.

I have made many attempts, by the use of Ross's $\frac{1}{8}$, and Powell and Lealand's $\frac{1}{25}$-inch object glasses, to discover how the wall is built up in the mature cotton fibre, but without success. Some concentric rings in cross sections, sketched in Plate VII., are apt to be mistaken for internal structure. They will be recognised as an optical effect, obtained by placing the illuminator out of focus, and especially when using gas light.

MORDANTING WITH THE ACETATES OF IRON AND OF ALUMINA.

Plate IV., A, shows side views of the ordinary cotton fibre which has been made to imbibe the pyrolignate of iron in the manner described at page 7, and then dyed in madder and soaped. The compound of madder and iron which forms this purple dye is so uniformly distributed over the cellular matter which it colours, that we can scarcely detect any point of full-grown fibre which it does not pervade. On the other hand, although the greater part of the dark markings of these fibres are due to irregularities of the surface corresponding with those of the undyed fibres, Plate I., there are other markings to be found in the centre of almost every fibre, which, after examining the cross sections of the same preparation at D, Plate VIII., and observing the clots which occur in the centre of many of them, will easily be recognised as accumulations of the black lake of madder and iron.

We must assume that in this process every cavity of the fibre has been filled with the iron solution; and we know that when that solution is evaporated to dryness, the acetate is gradually decomposed and converted into the hydrated peroxide of iron, which, by combining with madder, becomes the black or purple-lake already alluded to. The cavity in the centre (D, Plate VIII.) is sufficiently capacious, and admits solution enough to exhibit to us this lake in the form of a bulky black clot collected into one mass, altogether separate from, and sometimes scarcely touching, the bag which contains it. It is not too much to infer that in each of those innumerable though invisible cavities which exist throughout the body of the fibre, a similar process goes on, and that each enclosure, after imbibing its fill of the iron solution, contains first a parcel of the dried acetate, which soon becomes a clot of the hydrated peroxide, as distinct, in its degree, from the wall which surrounds it, as that which we are enabled to see in the central cavity. I need not repeat that the substance which is seen under the microscope to be black in the central opening, is the same with that which, in a state of still greater subdivision, gives a purple colour to the body of the fibre. At B, Plate IV., and at E, Plate VIII., are shown the effects of the same process applied to mature cotton previously mercerized. When acetate of alumina is employed instead of the iron solution, the only difference in the appearance is the substitution of red for purple.

Plate VI., No. 1, shows transverse sections of the ordinary

cotton fibre mordanted with acetate of alumina and dyed red. In depth of colour they are extremely unequal, of which the chief cause no doubt is the variety in the thickness of the slices; but there are always present also fibres comparatively unripe, and even well-formed fibres differ in the amount of the colour they receive. This inequality is nowhere more remarkable than in the cross sections and the side views of the most beautifully dyed turkey-red yarn, notwithstanding its perfectly uniform appearance to the naked eye in the aggregate.

Deep red specks, which are evidently clots of the red lake of alumina and madder, are seen occasionally occupying the otherwise void space in the heart of the fibre mordanted with acetate of alumina, but these occur to a much greater extent in cotton mordanted with mono-muriate of alumina, as will presently appear.

No. 2, Plate VI., shows the appearance of a fibre mordanted with acetate of alumina, and not fully dyed; that is, a fabric to which a sufficient quantity of madder had not been given to saturate all the alumina which it had received. It is only as the outer portions of the mordant become saturated that they allow the madder to pass inwards; and until that takes place, the fibre remains uncoloured in the centre.

Whether Thickening impedes the entrance of a Mordant into the Cotton Fibre.—I shall here remark that whether the mordant be applied to a piece of calico in the fluid state, or made nearly solid with an amylaceous or other thickening substance, it finds no difficulty in traversing the whole fibre. I have examined threads which have been soaked with a solution of acetate of alumina altogether fluid—comparing them with other threads which had been printed with the same solution made into a thick mucilage with gum-arabic, and with others again made into a paste with the flour of wheat, so thick that when applied to one side of a piece of bleached calico, it did not pass through to the other side; and on examining transverse sections of dyed specimens of these fibres, I found that such of them as had been reached by the mordant were in all these cases equally penetrated. The white centre was always due to a want of dye-stuff.

I am glad to be able to establish this fact,—an apparent impossibility which has been a stumbling-block to several of my friends. It is difficult, no doubt, without direct examination, to conceive of a capillary power so great, or that a solution rendered

so tenacious as to require considerable force to drive it through an opening of an inch in diameter, should be able, without any pressure at all, to pass into the interior of the cotton fibre, the pores of which cannot be detected by the most powerful microscope. In the latter case we have reason to believe that the solution leaves its farinaceous accompaniment at the entrance, and passes on; but a similar effect cannot be so readily supposed in the case of a mucilage.

Plate VII., B.—The *youngest fibre* bleached and mordanted with acetate of alumina, then dyed with madder, and afterwards soaped. A, The youngest fibres unbleached and similarly treated.

Plate V., B.—The *half-ripe fibre* unbleached, mordanted with acetate of alumina, dyed with madder, and soaped. When bleached, a great many fibres of the half-ripe cotton remain altogether colourless after having undergone the dyeing process, and the whole are much paler than the unbleached. C, The same half-ripe fibre bleached and mercerized, and then similarly treated.

The fibre *three-fourths ripe*, whether bleached or unbleached, (judging from the small specimen at my command), takes a dye, after mordanting with acetate of alumina, little if at all inferior to the mature cotton.

MORDANTING WITH MONO-MURIATE OF ALUMINA.

To prepare this solution, the sulphate of alumina (known as concentrated or cake alum) is decomposed by chloride of calcium, and the fluid purified from iron by means of ferrocyanide of potassium. For that purpose a solution of the ferrocyanide is added to the impure muriate of alumina so long as any precipitate is formed; and as the deposit does not separate by filtration, it is left to subside. Small floating particles, however, remain after the principal part of the prussian blue has gone down, and these are separated by albumen, a very small quantity of which collects them in the usual way of clarifying. The product is then divided into three equal parts. Two are decomposed by ammonia, and the precipitated alumina, after being filtered and washed, is added to the third portion, which redissolves it.

The mono-muriate of alumina thus formed has usually been employed for these experiments, of a specific gravity 1·125, at which it is strong enough to be converted into a thick magma by the addition of ammonia. The cotton is left to soak several hours in

this solution, after which it is washed in water, dyed in madder, and soaped. I shall describe the action of this compound upon the various fibres more particularly than its industrial importance would seem to merit, because it represents what appears to me to be an additional character not before recognised in the action of mordants upon cotton.

The *Youngest Fibre*, when bleached, takes no alumina from the solution of the mono-muriate. I have given a sketch, however (D, Plate VII.), for comparison, of fibres which have been subjected to the process. The same fibre unbleached (C, Plate VII.) takes exceedingly little. Many of the unbleached fibres remain destitute of colour, and others, probably more mature, take up a very small quantity of alumina, and they all take it in the peculiar way there represented—a layer of alumina between the walls of the fibre.

It is the cotton, however, in what I have called the *half-ripe stage* that furnishes the most remarkable example of the peculiar manner in which alumina is deposited in the fibre by immersion in the basic solution of that earth. I have endeavoured to picture its microscopic appearance in Plate V., A, the flat fibres being the same as those shown without dye in Plate II. The same preparation is represented in tranverse section, Plate VI., No. 7. Unlike the youngest fibre, the half-ripe cells are in such a state of growth that their walls readily separate to admit of the introduction of the fluids in which they may be immersed. When after two or three hours of such immersion, the cotton is washed in cold water, a quantity of hydrate of alumina is found separated from its solution, and retained by the fibre.

The circumstances are these:—The young fibre, an empty flattened bag, is placed in the basic solution, which soaks and more or less completely fills it. It is then put into water, or what Mr. Graham has called an atmosphere of water. The bag or cell wall acts the part of the septum described by him in experimenting on similar fluids, and the salt is decomposed. The crystalloid portion—the muriate of alumina—diffuses through the septum into the surrounding water, and the colloid hydrate of alumina remains within, gelatinized, no doubt, either spontaneously or by the traces of saline matter which are always present. The fibre itself, through which the aluminous solution has passed and repassed, retains no trace of the presence of alumina. It may be called a microscopic dialyser.

Many of these fibres seem as if a thin film of alumina had

originally been deposited within them over their whole length and breadth; and in all of them there is evidence of the deposit having shrunk to a great extent in both directions in the process of dyeing. It is remarkable that the alumina should adhere so slightly to the membrane which contains it, as thus to shift without difficulty from one part of it to another in the act of shrinking. The same remark applies to the clots found in the centre of full-grown cotton, whether the mordant of iron or alumina be applied from an acetic solution, or as in the case before us.*

By previous bleaching of this fibre, the quantity of alumina which it can receive is much diminished, but enough is admitted to form with it a most interesting microscopic object. In all cases the cell remains beautifully colourless and crystalline, enclosing its flakes of carmine; and the variety in the distribution of these flakes is infinite.

Along with these drawings are placed representations (D, Plate V.) of the same half-ripe fibre in the unbleached state, and swelled out by strong soda, previous to receiving the mordant; and they form examples not less remarkable of the action of the cotton fibre upon this salt. The opening in the centre appears to have been entirely filled with the clot, which (as it does with other fibres) has shrunk both in length and breadth in the subsequent processes. In the corresponding transverse sections (Plate VI., No. 8) pieces of the clot may often be seen scattered over the slide, having dropped out of their places, and lying near the aperture which had contained them.

When the half-ripe cotton is bleached previous to being mercerized, and then mordanted with mono-muriate of alumina and dyed (E, Plate V.), not only is the body of it much paler than the unbleached, but no such masses of colour reach the centre. In some instances a colourless fibre encloses a quantity of the red lake.

The effect of bleaching in diminishing the power of cotton to

* From the manner in which the mono-muriate of alumina acts upon cotton, it is evident that the process in which it is employed must be removed from the *1st Class* of dyeing processes, to which I assigned it in my second memoir, page 15, and of which indigo is the type, and placed in the *2nd Class*, as defined at page 5 of that memoir. The alumina is not attracted by the pores of the tissue, as indigo is. When dissolved in the termuriate, it passes into the interior of the fibre through these passages by ordinary capillary force, and when the fibre, with its contents, is subsequently placed in water, the alumina remains in its enclosure in consequence of the diffusive character of its solvent.

receive mordants is to be attributed to the boiling in weak solutions of quicklime and carbonate of soda to which the cotton is subjected, and not to the hypochlorite of lime, which is very sparingly used in the process of bleaching, nor to the sulphuric acid, which does not affect the mordanting. Hot alkaline solutions, though weak, matt together the young fibres, and close their passages against the admission of mordants. They have a similar tendency when applied to riper cottons, while that of strong caustic alkaline solutions is, as we have seen, to open them. Hypochlorites in excess also open the pores of ripe cotton, and, by enabling them to admit more mordant, greatly increase the intensity of the dye.

At No. 3, Plate VI., are cross-sections of ordinary cotton, mordanted with mono-muriate of alumina. Like the unripe fibres, they show that the salt had passed into the centre of the tube, and had been there decomposed.

MORDANTING WITH OXYCHLORIDE OF IRON.

The sesquichloride of iron, with the addition of an equivalent of sesquioxide of iron, form sa solution ($Fe_2Cl_3 + Fe_2O_3$) corresponding, in its action upon the cotton fibre, with the mono-muriate of alumina. It gives up its peroxide in a similar manner, and thus forms a mordant which, when dyed with garancin, produces upon the cotton a black or a purple colour, in proportion as the quantity of oxide which it has received is greater or smaller.

The oxychloride may readily be obtained by adding ammonia to 100 parts by weight of nitrate of peroxide of iron, of specific gravity 1·55, washing the precipitate, and re-dissolving it in 37½ parts hydrochloric acid of specific gravity 1·17.

The cotton is steeped for a couple of hours in this solution reduced to the specific gravity of from 1·03 to 1·07; after which it is placed in water, and washed before being dyed. The dye for this preparation of iron is garancin, which does not require soaping.

The effects are shown in Plate VIII. The unripe fibre, A, acts the part of a membrane or dialyser for decomposing the solution when placed in water, and as a bag for retaining, without being itself coloured by, the precipitated oxide, or its purple-lake. The same fibre B, while it has an equal power of admitting the solution into its interior, has likewise, by the mercerizing process, had cavities or enlarged pores formed in its wall; and each of these appears to

have taken its proportion of the iron, so as to produce, when dyed, a purple tube—the larger quantity of iron in the centre giving a black. With the ripe fibre, C, a quantity of the oxide has been retained in the hollow centre, and but little by the walls themselves.

EXPLANATION OF THE PLATES.

PLATE

I. Full-grown cotton, magnified about 400 diameters, as seen with Ross's $\frac{1}{8}$-inch object-glass, and mounted dry.

II. Unripe cotton.—Half-ripe cotton taken from an Algerian pod, which, when dry, was almost entirely closed; and along with them fibres in what I have described as the youngest stage.

III. Transverse sections of various conditions of the cotton fibre, as there described, and all as they appear when mounted (except No.2) in glycerin jelly.

IV. A, Full-grown cotton prepared with a mordant of pyrolignate of iron, then dyed in madder and soaped. At D, Plate VIII., will be found transverse sections of A.

B, The same as A, but steeped before mordanting in a strong solution of caustic soda. At E, Plate VIII., are transverse sections of B.

V. Half-ripe fibres with aluminous mordants, dyed in madder and soaped.

A, Mordanted with mono-muriate of alumina.

D, The same, but mercerized in the unbleached state before mordanting.

E E, The same, bleached and mercerized previous to mordanting.

B, Mordanted with acetate of alumina without being bleached.

C, Mordanted with acetate of alumina after having been bleached and mercerized.

VI. Transverse sections of the various fibres with aluminous mordants, dyed in madder and soaped.

VII. A and B, The youngest fibre mordanted with acetate of alumina, showing the effect of bleaching upon dead cotton in rendering it less capable of receiving a dye. C and D, which are mordanted with mono-muriate of alumina, give the same indication in an equally remarkable manner.

Transverse sections of mature cotton dyed chrome-orange, as seen with Powell and Lealand's $\frac{1}{25}$-inch, showing concentric rings—an effect of diffraction, not of structure.

VIII. A, The half-ripe fibre mordanted with oxychloride of iron, and dyed with garancin. A 2, Transverse sections of A, where the greater part of the lake is seen to be lodged in the hollow of the fibre.

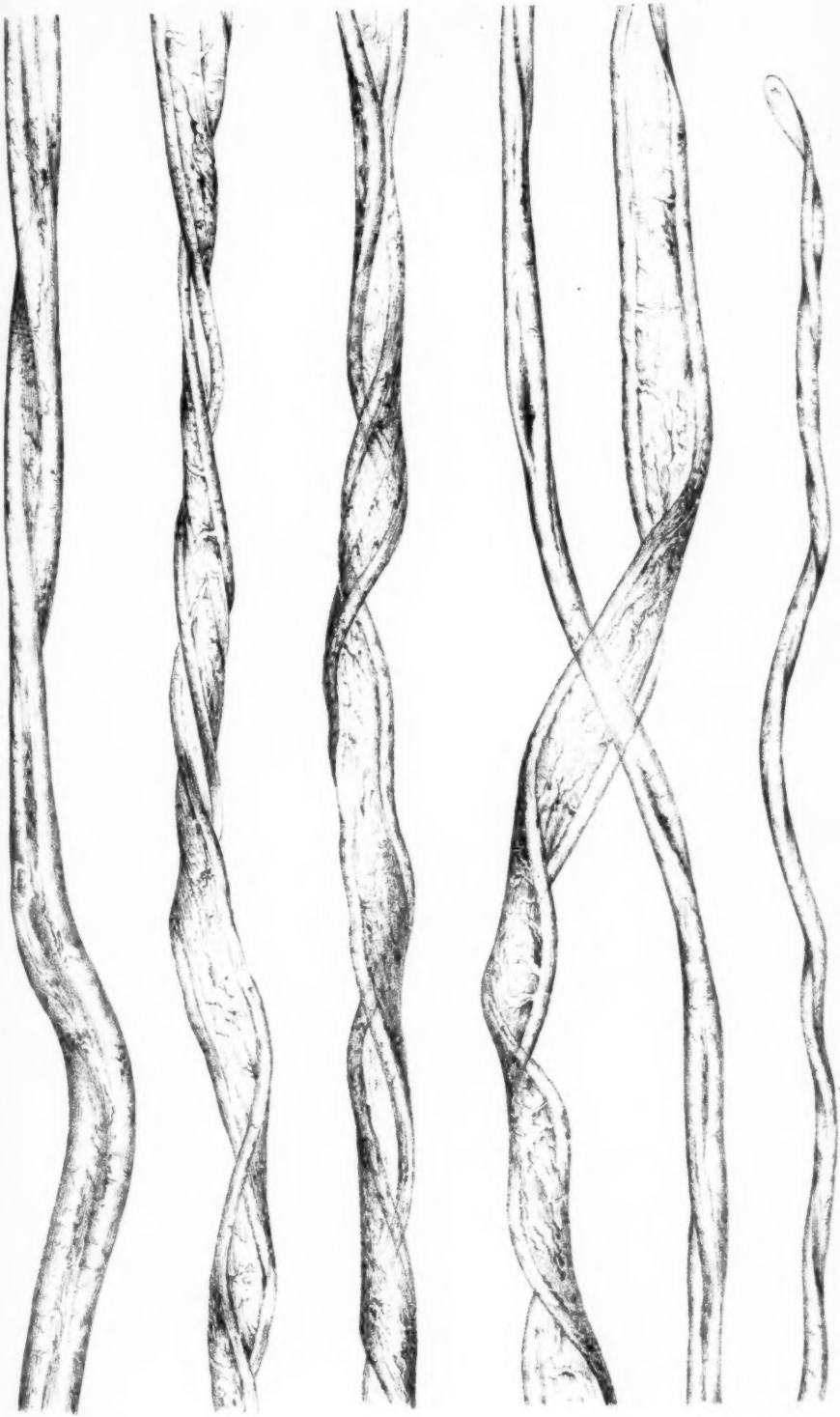
B and B 2, The half-ripe fibre mercerized, and then mordanted with oxychloride of iron, showing the effect of soda in opening the pores to admit the mordant into the body of the wall, and retain it there, as well as to allow of its passing through the wall into the central cavity.

C and C 2, The full-grown cotton mordanted with oxychloride of iron, and dyed in garancin.

D, Full-grown cotton mordanted with pyrolignate of iron, dyed with madder and soaped. Side views of the same preparation are given at A, Plate IV.

E, The same dye with mercerized cotton. Side views at B, Plate IV.

MATURE COTTON



E. Schneider Del.

Hanhart & Waldbauer Lith.

Masters & Macdonald Lith.

TRANSVERSE SECTIONS OF COTTONS

1 Mature Cotton

2 Mature Cotton, Mounted Dry

3 Mature Cotton Mercerised

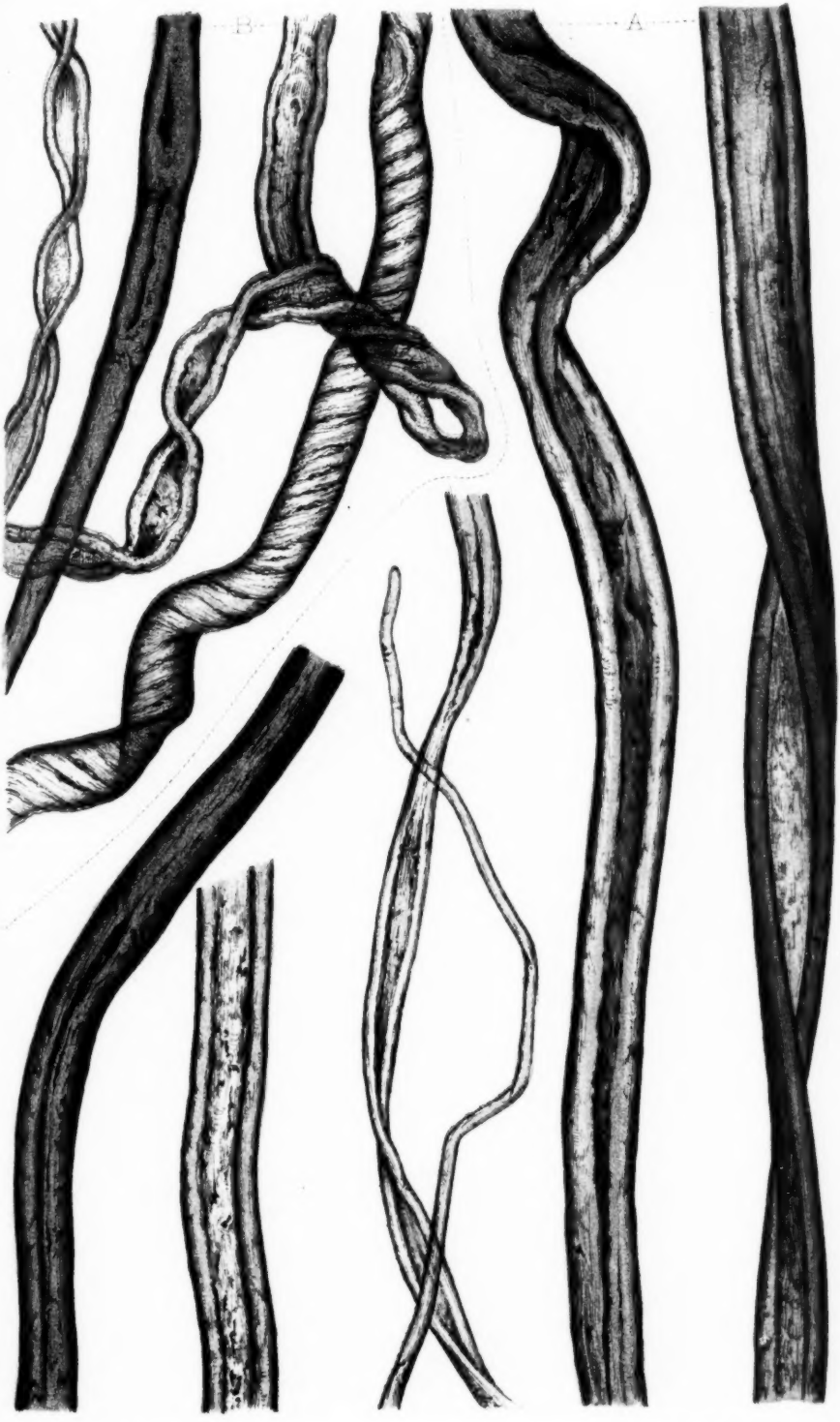
4 Half Ripe Cotton

5 Half Ripe Cotton Mercerised

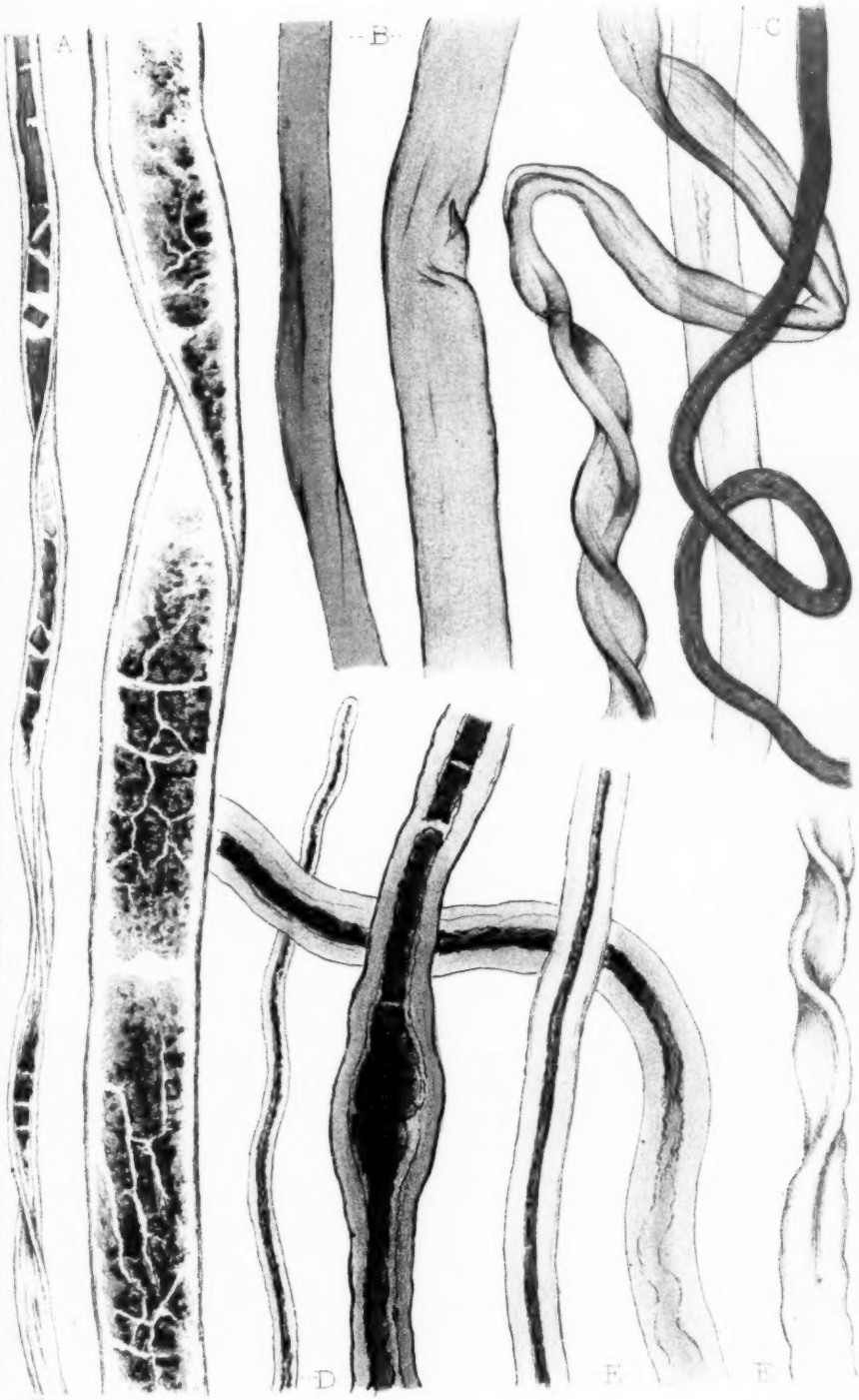
6 Cotton Fibre Ripe

7 Fibre of Cotton Ripe Mercerised

8 Fibre Cotton Ripe Cotton


B
A

COTTON FIBRES WITH THE LAKE OF ALUMINA & MADDER.



S. Roander Del.

Maclure & Macdonald's Lith.

TRANSVERSE SECTIONS WITH THE ALUMINOUS LAKE OF MADDER.

1. Mature Cotton Mordanted with Acetate of Alumina

2. As N°1 but deficient in quantity of Madder

3. Mature Cotton Mordanted with Mono Muriate of Alumina

4. Mature Cotton Mercerised – Acetate of Alumina

5. Mature Cotton Mercerised – Mono Muriate of Alumina

6. Cotton 3/4 the Pipe – Acetate of Alumina

7. Half Pipe Cotton – Mono Muriate of Alumina

8. Half Pipe Cotton Mercerised – Mono Muriate of Alumina

Un-Bleached — The Youngest Cotton very much [illegible] Bleached

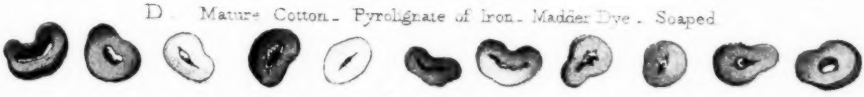
Un-Bleached — The Youngest Cotton [illegible] Bleached

Transverse Sections of Cotton, [illegible]

E. Schaller Del. [illegible]

COTTON FIBRES WITH THE LAKE OF IRON AND MADDER

D. Mature Cotton. Pyrolignate of Iron. Madder Dye. Soaped



E. Same as D, but first Mercerised

E Scandler Delt.

Maclure & Macdonald Lith.

L.—*On a new method of producing the Mercury compounds of the Alcohol-radicles.*

By E. Frankland, Esq., F.R.S., Professor of Chemistry at the Royal Institution of Great Britain; and B. F. Duppa, Esq.

The organo-compounds of mercury have hitherto been prepared by one of the two following processes:—I. Mercury and the iodide of the alcohol-radicle were submitted to the action either of sunlight or diffused daylight, when direct union of the two bodies took place, and the iodo-mercuric compound was the result.*

$$\dagger Hg + \left.\begin{matrix} C_nH_{2n+1} \\ I \end{matrix}\right\} = Hg\left\{\begin{matrix} C_nH_{2n+1} \\ I \end{matrix}\right.$$

II. Mercuric chloride was mixed with the zinc-compound of the alcohol-radicle, when there was formed an organo-mercuric compound, containing either two atoms of the alcohol-radicle, or one atom of such radicle and one of chlorine, the nature of the product being determined by the employment of one or other of the ingredients in excess:‡

$$Zn\left\{\begin{matrix} C_nH_{2n+1} \\ C_nH_{2n+1} \end{matrix}\right. + Hg\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. = Hg\left\{\begin{matrix} C_nH_{2n+1} \\ C_nH_{2n+1} \end{matrix}\right. + ZnCl_2.$$

$$Zn(C_nH_{2n+1}) + 2HgCl_2 = 2\left(Hg\left\{\begin{matrix} C_nH_{2n+1} \\ Cl \end{matrix}\right.\right) + ZnCl_2.$$

Organo-mercuric compounds can also be obtained by treating the haloid mercuric body of the first process by the zinc-compound of an alcohol-radicle. Iodo-mercuric ethide and methide are obtained with considerable facility by the first process, but the corresponding compound of amyl has only hitherto been procured in quantities so minute as barely to suffice for its identification. On the other hand, mercuric ethide and methide require for their preparation large quantities of the zinc-compounds of the respec-

* Phil. Trans., 1852, p. 436.

† The atomic weights used in this paper are the following:—
C = 12; H = 1; Hg 200; Cl = 35·5; I = 127; Zn = 65.

‡ Phil. Trans., 1858, p. 163, and 1859, p. 417.

tive radicles, whilst the production of mercuric amylide has never yet been attempted, on account of the impossibility of preparing zinc-amyl in sufficient quantity. Under these circumstances a new and less troublesome reaction for the preparation of these bodies will probably not be unacceptable to chemists, and we therefore place on record the following, which recently came under our notice during the prosecution of researches upon another subject:—

Action of Sodium-amalgam upon Iodide of Methyl in presence of Acetic Ether.

When iodide of methyl is placed in contact with sodium-amalgam, no perceptible action takes place at ordinary temperatures, even after prolonged digestion, but on the addition of a few drops of acetic ether, the amalgam is immediately attacked, and a brisk action, attended by a considerable elevation of temperature and a slight evolution of gas, goes on for some time. A mixture of ten parts by weight of iodide of methyl and one part of acetic ether was treated with sodium-amalgam, the flask containing these ingredients being alternately agitated to promote the reaction, and plunged into cold water to moderate the rise in temperature. To the neck of the flask was attached a small Liebig's condenser, to arrest the vapour of iodide of methyl, which would otherwise have been carried away with the escaping gas.

The completion of the reaction is known by the subsidence of the temperature, and by the absence of more than traces of precipitated iodine, when a few drops of the clear liquid remaining in the flask are boiled with nitric acid. When the quantity of iodide of sodium formed has so increased as to render the ethereal liquid pasty, thus preventing a sufficiently intimate contact with the amalgam, it is advisable to place the flask in a water-bath, and to distil off the more volatile portion of the contents, to be again acted upon with fresh amalgam. If this distillation be not performed until the product has become decidedly thick and pasty, it will not be necessary to repeat it, as the distillate will remain sufficiently fluid up to the termination of the reaction. At the conclusion of the operation, the residues in the flasks are mixed with water and submitted to distillation in an oil-bath, the temperature of which need not be raised above 110° Cent.

The ethereal distillate, after separation from the water which accompanied it, was first agitated with alcoholic potash to remove acetic ether, and afterwards well washed with water; it then exhibited the boiling point and other properties of mercuric methide. A portion of it was dissolved in alcohol, and treated with iodine so long as the latter failed to produce permanent colour in the liquid. The crystalline magma of mercuric iodo-methide thus obtained was thrown upon a filter, washed with alcohol, and re-crystallized from hot methylic alcohol, in which it is much more soluble than in ether or ethylic alcohol. The beautiful nacreous crystals were pressed between folds of blotting paper, dried over sulphuric acid in vacuo, and submitted to analysis with the following results:—

I. ·7942 grm. burnt with oxide of copper and metallic copper in a current of air and oxygen, gave ·1032 grm. of carbonic acid, ·0754 grm. water, and ·4617 grm. of mercury.*

II. ·9410 grm. treated as before gave ·0985 grm. water, and ·5482 grm. mercury. (In this analysis the carbonic acid determination was lost.)

III. ·5480 grm. dissolved in methylic alcohol and precipitated with nitrate of silver gave ·3761 grm. iodide of silver.

These numbers agree closely with those calculated from the formula of mercuric iodo-methide:

$$Hg \left\{ \begin{matrix} CH_3 \\ I \end{matrix} \right.$$

* We found the following a very accurate and convenient method for the analysis of this and the following mercurial compounds. The front extremity of the combustion tube is drawn out, so as to form a narrow tube about two or three inches long and of such a diameter as to permit of direct union with the sulphuric-acid tube by means of a caoutchouc joint. Three inches further back, the combustion tube is again drawn out, and the two contracted portions bent, so as to form a kind of U tube for the reception of the mercury and water. At the conclusion of the combustion, and whilst the current of air is still passing, the contracted part of the tube nearest to the oxide of copper is withdrawn somewhat from the furnace, and after carefully chasing with a spirit-lamp into the U-shaped tube any globules of mercury that may have lodged in the contracted neck, the latter is sealed through by means of a blowpipe-flame. The potash apparatus having been previously detached, a second sulphuric-acid tube is substituted in its place, and the free end connected with a good air-pump. (These sulphuric-acid tubes are each constructed of a single piece of glass, the delivery tubes being sealed on after filling with pumice stone.) A

	Calculated.		Found.			
			I.	II.	III.	Mean.
C	12	3·51	3·54	..	..	3·54
H_3....	3	0·88	1·05	1·15	..	1·10
Hg....	200	58·48	58·13	58·26	..	58·20
I	127	37·13	..	..	37·07	37·07
	342	100·00				99·91

The formation of mercuric methide from iodide of methyl and sodium amalgam may, therefore, be thus represented:

$$2\,CH_3I + Na_2 + Hg = Hg\begin{cases}CH_3\\CH_3\end{cases} + 2\,NaI.$$

Action of Sodium-amalgam upon Iodide of Ethyl in presence of Acetic Ether.

The phenomena in this reaction are precisely similar to those observed in the last; iodide of ethyl and acetic ether, in the proportion of ten parts by weight of the former to one of the latter, were poured upon sodium-amalgam, and the mixture alternately agitated and cooled as before. The mixture became pasty, and required distillation as in the last reaction. The product was mixed with water, when it separated into two layers, and the ethereal liquid either floated or sank in the aqueous solution of iodide of sodium, according to the degree of concentration of the latter. It was then successively treated with alcoholic potash, washed with water, dried over chloride of calcium, and rectified,

vacuum must now be made in the tubes and maintained for about an hour, at the end of which time the whole of the water will have passed from the U tube into the sulphuric-acid tube without any application of heat to the former. The second sulphuric-acid tube is used to prevent moisture gaining access to the first through any leakage in the pump. The usual process of separating water from mercury by a current of dry air is excessively tedious at ordinary temperatures, besides being liable to very considerable error through inequality of the two desiccations of the current of air; whilst if the operation be shortened by the application even of very gentle warmth, mercury is infallibly carried into the sulphuric-acid tube. The method now described is not open to either of these sources of error, and it might, doubtless, be applied with advantage in all analytical operations where water has to be separated from mercury. After the desiccated U-tube has been weighed, its sealed extremity is heated in a fine blowpipe flame, whilst a gentle pressure of air is applied from the opposite end. An opening is thus made in the sealed extremity without any loss of glass, and the mercury can now be expelled by heat and a current of air in the usual manner.

when it was found to consist of pure mercuric ethide, boiling constantly at 159° Cent., and possessing properties identical with that first prepared by Buckton.

Treated with alcoholic solution of corrosive sublimate in excess, it yielded a copious crystalline precipitate of mercuric chloroethide, which, after being separated as much as possible from the mother-liquor, dissolved in boiling alcohol and, precipitated by water, furnished a white crystalline mass. This was collected upon a filter, well washed with hot water, in which it is but slightly soluble, dried over sulphuric acid in vacuo, and submitted to analysis:

I. ·8744 grm. gave ·2760 grm. carbonic acid, ·1445 grm. water, and ·6594 grm. mercury.

II. ·4672 grm. gave ·0881 grm. water and ·3528 grm. mercury.

III. ·2584 grm. gave ·1948 grm. mercury.

IV. ·3678 grm. dissolved in alcohol, and precipitated with nitrate of silver, gave ·2017 grm. chloride of silver. The numbers deduced from the formula—

$$Hg \begin{cases} C_2H_5 \\ Cl \end{cases}$$

coincide closely with those calculated from the above determinations, as is seen from the following comparison:

	Calculated.		Found.				
			I.	II.	III.	IV.	Mean.
C_2 ..	24	9·07	8·61	..	..	..	8·61
H_5 ..	5	1·88	1·84	2·10	..	..	1·97
Hg ..	200	75.62	75·41	75·51	75·39	..	75·44
Cl ..	35·5	13·43	..	..	..	13·55	13·55
	264·5	100·00					99·57

The following equation expresses the formation of mercuric ethide in the above reaction:—

$$2\,C_2H_5I + Na_2 + Hg = Hg \begin{cases} C_2H_5 \\ C_2H_5 \end{cases} + 2\,NaI.$$

Action of Sodium-amalgam upon Iodide of Amyl in presence of Acetic Ether.

As the organo-compounds of amyl can only be obtained in very minute quantities by the reactions hitherto known, it is satisfactory to find that the process we are now about to describe is capable of yielding them in abundance. When five parts by weight of iodide of amyl and one of acetic ether are placed in contact with sodium-amalgam and agitated, a brisk action immediately commences, and the application of external cold is required to keep down the temperature of the mixture; but there is here no necessity for any intermediate distillation, as the liquid retains sufficient fluidity to allow the reaction to complete itself. The resulting product was submitted to distillation in a water-bath to separate the acetic ether. A current of steam was then passed into the retort until about one-half of the heavy liquid had passed over. The residual ethereal liquid washed with water, and dried over chloride of calcium, was submitted to analysis, and yielded the following numbers:—

I. ·4870 grm. gave ·6263 grm. carbonic acid, ·2817 grm. water, and ·2849 grm. mercury.

II. ·6363 grm. gave ·3586 grm. water and ·3725 grm. mercury.

These numbers agree with the formula—

$$Hg \left\{ \begin{matrix} C_5H_{11} \\ C_5H_{11} \end{matrix} \right.$$

as indicated by the annexed comparison:—

	Calculated.		Found.		
			I.	II.	Mean.
C_{10}	120	35·09	35·07		35·07
H_{22}	22	6·43	6·43	6·26	6·35
Hg	200	58·48	58·50	58·54	58·52
	342	100·00	100·00		99·94

The action of sodium-amalgam upon iodide of amyl may be thus expressed:—

$$2C_5H_{11}I + Na_2 = Hg\left\{ \begin{matrix} C_5H_{11} \\ C_5H_{11} \end{matrix} \right. + 2NaI.$$

Mercuric amylide is a colourless, transparent, mobile liquid,

possessing a very faint amylic odour, and leaving a persistent taste upon the palate, resembling that produced by other organo-mercurial compounds. It cannot be distilled, even in vacuo, without partial decomposition. Although it can bear a temperature of 140° Cent., yet long before its boiling point is reached, mercury separates from it in considerable quantity. This behaviour under the influence of heat might be expected from the analogous deportment of mercuric ethide, which, as was observed by Buckton,* is decomposed, with slight explosion, at a temperature of 205° Cent. Mercuric amylide can, however, be distilled with water without decomposition. It is insoluble in water, and very slightly soluble in alcohol, but dissolves readily in ether. Its specific gravity is 1·6663 at 0° Cent. Exposed to the air it suffers no oxidation, but when allowed to fall into chlorine, it immediately produces dense white fumes of mercuric chloro-amylide. Brought into contact with solid iodine, it hisses like red-hot iron immersed in water. The reaction with bromine is still more violent.

An ethereal solution of mercuric amylide, treated first with alcoholic solution of iodine and then with solid iodine, nearly solidifies to a crystalline mass of mercuric iodo-amylide, iodide of amyl being at the same time produced.

$$Hg\left\{\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\right. + I_2 = Hg\left\{\begin{matrix}C_5H_{11}\\I\end{matrix}\right. + C_5H_{11}I.$$

The crude mercuric iodo-amylide was washed with weak alcohol, pressed between folds of blotting paper, and re-crystallized from hot alcohol, when it was deposited in small pearly scales, which dried in vacuo over sulphuric acid, and submitted to analysis, yielded the following results:—

I. ·6843 grm. gave ·3740 grm. carbonic acid, ·1905 grm. water, and ·3445 grm. mercury.

II. ·4096 grm. dissolved in alcohol, and precipitated with nitrate of silver, gave ·2418 grm. iodide of silver.

III. ·7154 grm. gave ·3896 grm. carbonic acid, ·1806 water, and ·3608 grm. mercury.

These numbers agree closely with the formula—

$$Hg\left\{\begin{matrix}C_5H_{11}\\I\end{matrix}\right.$$

* Phil. Trans., 1858, p. 163.

as is seen from the following comparison—

	Calculated.		Found.			
			I.	II.	III.	Mean.
C_5.....	60	15·08	14·90		14·85	14·87
H_{11}	11	2·76	3·09		2·80	2·95
Hg	200	50·25	50·34		50·43	50·38
I	127	31·91		31·89		31·89
	398	100·00				100·09

Mercuric iodo-amylide crystallizes from boiling alcohol in minute brilliant scales, which are not very readily soluble in alcohol but largely so in ether. One curious circumstance we noticed with regard to these crystals is, that if to a boiling saturated alcoholic solution a few drops of alcoholic potash be added, and the liquid be allowed to cool, no crystals appear for some time, and then, instead of the microscopic scales obtained in the first instance, large pearly plates are produced; these plates washed with water, and dissolved in alcohol, reproduce small crystals resembling the first crop. Notwithstanding the great difference in appearance between these and the former crystals they are identical in composition, as seen from the foregoing analytical results, analyses Nos. I and II having been made with the minute scales, whilst No. III was performed with the large plates. Mercuric iodo-amylide is slightly soluble in boiling water, from which it separates on cooling in minute crystals, which appear as an opalescent cloud in the liquid. When fused, iodo-amylide appears to undergo no decomposition, so long as the temperature is not raised much above its melting point, which is 122° Cent. At 140° it begins to turn yellow, from the formation of proto-iodide of mercury; on cooling it congeals to a white crystalline mass, having the appearance of stearin. In a current of air moderately heated, mercuric iodo-amylide may be sublimed without change. It is at most but partially decomposed by an alcoholic solution of potash.

Mercuric chloro-amylide ($HgC_5H_{11}Cl$) is readily obtained by treating mercuric amylide with alcoholic solution of corrosive sublimate in excess. It closely resembles the iodo-amylide in its properties, is insoluble in water, but very freely soluble in hot alcohol and ether. From its alcoholic solution it crystallizes in beautiful hair-like needles, which can be sublimed at a gentle heat

without decomposition. It fuses at 86° Cent., and has the appearance of a heavy oil, perfectly limpid and colourless. It retains any excess of corrosive sublimate with the greatest obstinacy, repeated washings with alcohol and water being incompetent to remove it. The only effectual way of purification we have yet found is to dissolve it repeatedly in alcohol and reprecipitate with water.

·5164 grm. thus purified gave ·2364 grm. chloride of silver, which agrees closely with the theoretical number:

	Calculated.		Found.
C_5	60	19·57	
H_{11}	11	3·58	
Hg.....	200	65·27	
Cl.....	35·5	11·58	11·32
	306·5	100·00	

Action of Sodium-amalgam on Iodide of Hexyl in presence of Acetic Ether.

Professor Wanklyn having kindly furnished us with a specimen of iodide of hexyl prepared by acting upon mannite with hydriodic acid, and which, as he has pointed out, yields an anomalous hexylic alcohol, we submitted it to the reaction described in the preceding pages.

Anomalous iodide of hexyl is readily acted upon by sodium-amalgam in the presence of acetic ether; but amongst the products formed, there is no trace of an organo-mercurial compound, a result which would indicate that this reaction might be conveniently employed to distinguish between the normal and abnormal iodides of the alcohol-radicles, the presence of an organo-mercurial compound, even in minute quantity, being readily traced by the addition of a small fragment of iodine to a drop of the liquid on a watch-glass, when the mercuric-iodo-compound is at once formed and crystallised.

Action of Sodium-amalgam on Hydriodic Acid in presence of Acetic Ether.

The extreme facility with which methyl, ethyl, and amyl are made to combine with mercury in the above reactions induced us to hope that the substitution of the iodides of those radicals by

hydriodic acid would furnish mercuric hydride, a body which could not fail to be of the highest interest in connection with organic research. Repeated experiments made under varied conditions have however failed to produce even traces of such a body. Hydriodic acid is very soluble in acetic ether, and sodium-amalgam acts readily upon the solution, but pure hydrogen only is apparently evolved; at all events no trace of mercuric hydride accompanies it.

We have not been able to ascertain the part played by the acetic ether in the above reactions; it can scarcely be that of a solvent alone, since the iodide of sodium formed is nearly insoluble in it. One thing, however, appears to be certain, viz., that at the conclusion of the reaction the acetic ether remains in undiminished quantity. Such contact actions, however, have almost invariably, when closely scrutinized, been proved to depend upon collateral chemical affinity, and such is also probably the case in the present instance, although it is difficult to conceive in what direction the affinity is exerted.

Ethylic ether, when substituted for acetic ether, fails to produce the desired effect, but, as might be anticipated, formic ether and acetate of methyl are quite as efficacious as acetic ether in inducing the formation of the organo-mercurial compounds. We have ascertained that the mercuric ethide, formed by the action of sodium-amalgam upon a mixture of iodide of ethyl and acetate of methyl, contains no trace of mercuric methide.

By the reactions described in the foregoing pages, it is easy to prepare in a short time large quantities of the mercury-compounds of methyl, ethyl, and amyl. The only precaution necessary to be observed is the proper proportion of sodium in the amalgam, which can scarcely be too small, especially for the lower members of the series, and it is remarkable that amalgams containing small proportions of sodium appear to act more energetically than those in which the alkali-metal is present in larger quantity. If a solid or semi-solid amalgam be employed, the reaction proceeds in quite a different manner, and will form the subject of a separate communication. The proportions we recommend for the production of organo-mercurial compounds are 1 part of sodium to 500 parts of mercury.

As the mercury accumulates in the flasks, it must be pipetted off and re-amalgamated with sodium. When working upon a large scale, it is advisable in all cases to distil off the acetic ether as far as possible before adding water to the result of the reaction.

The acetic ether thus separated, together with the small quantity of organo-mercurial compound which it contains, may then be advantageously used in a future operation.

LI.—*On the Chemical Constitution of the so-called Alcohol-Radicles.*

By C. Schorlemmer.

Assistant in the Laboratory of Owens College, Manchester.

The isomeric members of the two groups into which the hydrocarbons of the general formula C_nH_{2n+2} are, according to their formation, divided, namely the hydrides and the radicles, resemble each other very closely; the only distinct difference in their physical properties, which is known to exist, is the disagreement of their boiling points. Wurtz has, however, lately noticed a similar disagreement in the case of the boiling points of several hydrides having an identical composition, and he assigns to this property the name of physical isomerism.* With respect to their chemical properties, the members of the hydride group alone have been lately more closely investigated; they yield by the action of chlorine, as first substitution-product, the corresponding chlorides. Much less is known concerning the products obtained by the action of chlorine on the radicles. All that Frankland and Wurtz have shown in this respect is that chlorine may be substituted for hydrogen, but only compounds containing 2 or 4 atoms of chlorine have been obtained. Frankland has further shown that by the action of two volumes of chlorine on one volume of methyl, a gas of the composition $C_2H_4Cl_2$ is formed, whilst the isomeric hydride of ethyl yields, under the same circumstances, a liquid having the same composition. Hence, it has been generally concluded, that the radicles are not the homologues of marsh gas, as Laurent and Gerhardt first supposed.†

The following communication contains the first results of an investigation on the derivatives of the radicles; my chief object was to try to replace one atom of hydrogen by chlorine, and to compare these chlorine-compounds with those derived from the hydrides. As starting point, I chose the mixed radicle ethyl-amyl,

* Compt. rendues., li., 1164.

† Chem. Soc. Quar. J., iii, 323.

which is isomeric with hydride of heptyl C_7H_{16}, and the radicle amyl $C_{10}H_{22}$, which substances were obtained, according to Wurtz's method, by the action of sodium on a mixture of the iodides of ethyl and amyl.

1. *Ethyl-Amyl.*

If a current of chlorine is passed into ethyl-amyl containing a small quantity of iodine, the chlorine is completely absorbed, the liquid becoming hot and giving off hydrochloric acid. If the action of the chlorine is interrupted before the whole of the hydrocarbon is attacked, and the chlorinated liquid is subjected to repeated fractional distillations, two compounds of constant boiling point are obtained, a larger quantity of a liquid boiling at 150°C., and a smaller quantity of a liquid which boils at about 190°C.

The first of these compounds is identical with chloride of heptyl, which I have already described in a former communication.* It possesses the same boiling point and the same characteristic properties. The following analyses show that it has the same composition :—

(1) 0·3327 substance gave 0·3578 chloride of silver.
(2) 0·1932 substance gave 0·1875 chloride of silver and 0·0140 metallic silver.

	Calculated.		Found.	
			I.	II.
C_7	84	62·45	—	—
H_{15}	15	11·15	—	—
Cl	35·5	26·40	26·60	26·39
	134·5	100·00		

The identity of this chloride with chloride of heptyl was further proved by heating it with an alcoholic solution of sulphhydrate of potassium in a sealed tube, and converting it thus into the corresponding sulphhydrate, which was compared with sulphhydrate of heptyl obtained in the same manner from chloride of heptyl. Both are colourless liquids, boiling at 155—158°C, possessing a mercaptanlike as well as an aromatic odour, and showing all the characteristic reactions of the mercaptans.

0·1955 of the sulphhydrate derived from ethyl-amyl gave, by

* Chem. Soc. J., xv, 419.

the method of sulphur-determination proposed by Carius, 0·3470 sulphate of barium, corresponding to 24·38 % of sulphur, whilst the formula $C_7H_{16}S$ requires 24·24 %.

The liquid boiling at about 190°C has the composition $C_7H_{14}Cl_2$, as the following chlorine-determination shows:—

0·1775 of substance gave 0·2890 chloride of silver and 0·0085 metallic silver.

		Calculated.	Found.
C_7	84	49·71	—
H_{14}	14	8·28	—
Cl_2	71	42·01	41·85
	169	100·00	

This compound is therefore the *monochlorinated chloride of heptyl*, and no doubt identical with bichloride of œnanthylene, boiling at 191°C., which Limpricht prepared by acting with pentachloride of phosphorus on œnanthol,* as, according to Beilstein, the monochlorinated chloride of ethyl is identical with the bichloride of ethylidene,† which compounds are obtained in an analogous manner to those above mentioned.

2. *Amyl.*

Amyl behaves towards chlorine in exactly the same manner as ethyl-amyl does. From the chlorine substitution-products a large quantity of a liquid was obtained, boiling at about 200°C., and possessing the composition $C_{10}H_{21}Cl$.

(1) 0·2070 substance gave 0·1575 chloride of silver and 0·0075 metallic silver.

(2) 0·1890 substance gave 0·1355 chloride of silver and 0·0120 metallic silver.

		Calculated.	Found.	
			I.	II.
C_{10}	120	68·00	—	—
H_{21}	21	11·89	—	—
Cl	35·5	20·11	20·08	20·01
	176·5	100·00		

Wurtz obtained, by the action of chloride of zinc on amylic alcohol, a hydrocarbon having the composition of amyl, boiling at

* Ann. Ch. Pharm., ciii, 80. † Ann. Ch. Pharm., cxiii, 110.

155—157°C, and to which he gives the name of *hydride of diamyl*. From this hydride he prepared the chloride of diamyl, which boils between 190—200°C.* Pelouze and Cahours isolated from American petroleum a hydrocarbon of the same composition. The boiling point of this hydride of rutyl, as they call it, is 160—162°, and that of the chloride of rutyl 204—206°.†

It appears as if these two hydrides were identical with amyl; they certainly yield identical chlorides. The slight disagreement of the boiling points may be easily explained by the great difficulty which exists in isolating a product of constant boiling point from a mixture containing a large number of similar compounds.

To the above compounds the name of *decatyl-compounds* might be given.

Whether the greater disagreement, which is found in the boiling points of other isomeric bodies of this series, depends only on an admixture of impurities, which, as I have shown in the case of hydride of amyl, changes the boiling point considerably,§ or whether two or more series of these hydrocarbons exist, which show a physical isomerism and chemical identity, must be decided by future investigations. I may remark that such a difference in the boiling points has also been found in the olefine series. Some of the hydrides which I have described in a former paper possess a higher boiling point than their isomers, which were previously known. As I had purified them by means of the strongest acids, I thought it might be possible that the boiling point had been raised by the action of the latter. To decide this question, I added to some ethyl-amyl, which boiled constantly at 88°C., a large excess of a mixture of strong sulphuric and nitric acids. The liquids were left in contact for a fortnight, and repeatedly shaken. Very little action took place during that time; the ethyl-amyl was then removed from the acids, washed with water, dried over potash, and distilled over sodium; the boiling point was not altered, the whole of the liquid passing over at 88°C.

From the above results of this investigation, I venture to draw the conclusion, that no chemical difference exists between hydrides and radicles, at least amongst the higher members of this series, and that the formation of the latter is a real synthesis and quite analogous to the synthesis of amylene, which Wurtz effected by the action of zinc-ethyl on iodide of allyl,‖ and that of

* Compt. rend., lvi, 1246. † Compt. rend., lvi, 512; lvii, 68.
§ Proceed. Lit. Phil. Soc., Manchester, March, 1863. ‖ Compt. rend., liv. 387.

amylene and propylene from zinc-ethyl and chloroform, as discovered by Beilstein and Rieth.*

If these views are correct, a number of important questions present themselves for investigation. As I have already mentioned, methyl and hydride of ethyl show a different chemical deportment. How do the compounds between C_2H_6 and C_7H_{16} behave? Do only the two lowest isomers of this series give different derivatives, or do others show a similar disagreement, and with what member does this difference cease, or does it perhaps become less the higher the compound is placed in the series?

By means of the synthesis of these homologous bodies, we are in a position to obtain, in a pure state, the highest members of the series, which cannot be isolated by fractional distillation, and thus we may light up the somewhat dark region of the so-called paraffins.

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Another question which may be asked is, can we substitute in hydrocarbons of other series, hydrogen by methyl, ethyl, propyl, and so on, and thus obtain a series of homologues of these hydrocarbons, and in what relation do these homologues stand to previously known homologues? Is, for instance, phenyl-methyl identical with toluol, or only isomeric; do its derivatives belong to the tolyl group or benzyl group, or are they only isomers of both?

Instead of building up homologous series by substitution of hydrogen by methyl, ethyl, and so on, it may be possible to combine two atoms of a monatomic radicle with one atom of a diatomic, and to thus obtain, from ethyl-compounds, hydride of hexyl:

$$C_2H_4I_2 + 2C_2H_5I + 4Na = C_6H_{14} + 4NaI.$$

The so-called radicles of other series appear to show the same deportment as those of the series C_nH_{2n+2}. Fittig obtained, by the action of sodium on monobrominated benzol, the hydrocarbon $C_{12}H_{10}$, which he regards as the radicle phenyl. This body stands in the same relation to benzidine $C_{12}H_{12}N_2$, as benzol C_6H_6 to phenylene-diamine $C_6H_8N_2$.† The formation of this so-called phenyl appears as a synthesis of a member of the series C_nH_{2n-14}.

I hope soon to be able to lay before the Society a further communication, giving information respecting some of the above questions.

* Ann. Ch. Pharm., cxxiv., 242. † Ann. Ch. Pharm., cxxiv., 275.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 15th, 1863.

Col. Ph. Yorke, Vice-President, in the Chair.

The following were elected Fellows of the Society:—

John Noble, Esq., Working Men's College, Halifax; James Liebig Muspratt, Esq., 31, Mornington-road, Regent's Park; William Spiller, Esq., Atlas Chemical Works.

The following papers were read:—

"On the Atomic Weight of Cobalt:" by Dr. W. J. Russell.

"On the Action of Sulphuric Acid upon Lead:" by Messrs. F. Crace Calvert, and R. Johnson.

Dr. Frankland made a verbal communication on the Synthesis of Leucic Acid.

February 5th, 1863.

Dr. Hofmann, President, in the Chair.

The following were elected Fellows of the Society:—

R. R. Carew, Esq., 2, Upper Hyde Park Gardens; Dr. Reginald Thompson, M.B., 4, Upper Belgrave-street; Alfred Hutchison Smee, Esq., Finsbury Circus; H. P. Meader, Esq., George-street, Haslingden, Lancashire.

The following papers were read :—

"On the formation of Phenic and Benzoic Acids from Benzol:" by A. H. Church, B.A.

"On the Analysis of Red Chalk:" By A. H. Church, B.A.

"On the Atomic Weight of Nickel:" by Dr. J. W. Russell.

"Note on the Bicarbonate of Ammonia of the Chinca Isles:" by Dr. T. L. Phipson.

"Remarks on the Proposed Application of the Soap-test to the Quantitative Analysis of Water:" by Dr. B. H. Paul.

February 19th, 1863.

Col. Ph. Yorke, Vice-President, in the chair.

The following were elected Fellows of the Society:—

Joseph Green, Esq., 22, Colliergate, York; Charles Robert Clarke Titchborne, Esq., Apothecaries' Hall, Dublin; J. A. Wanklyn, Esq., Heidelberg; Robert Gibson West, Esq., 23, Lombard-street; John E. Woods, Esq., F.R.G.S., 1, Victoria-street, Westminster.

David Brown, Esq., Apothecaries' Hall, London, was elected an Associate of the Society.

The Chairman announced the names of the retiring President, Vice-President, and members of Council, and of the Fellows recommended by the Council for election in their places.

Dr. Hofmann read a paper "On Formamide."

March 5th, 1863.

Dr. Williamson, Vice-President, in the chair.

J. H. Atherton, Esq., of Nottingham, was elected a Fellow of the Society.

Dr. Gilbert delivered a lecture "On the Assimilation of Nitrogen by Plants."

March 19th, 1363.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society :—

Robert Warington, Jun., Esq., Cirencester; George Warington, Esq., Apothecaries' Hall; William Crossley, Esq., Ormsby Iron Works, Middlesborough-on-Tees; J. Robert Colman, Esq., Rockland House, King's-road, Clapham Park; William Bath Kemshead, Esq., M.A., Ph.D.

T. A. Malone, Esq., Clapham, was elected an Associate of the Society.

The following papers were read :—

"On the Chinoline and Leucoline Series:" by C. Greville Williams, Esq.

"On the Spontaneous Conversion of Gun-cotton into Pectic and Parapectic Acids:" by Dr. Edward Divers.

"On the Composition of some Native Coppers:" by Professor F. A. Abel.

"Note on Oxamide:" by Dr. Attfield.

Anniversary Meeting, March 31st, 1863.

Dr. Hofmann, President, in the chair.

The following Report was read by the President :—

In the career of a society, as in the life of an individual, a stage must sooner or later be reached, when the rate of development will contract, and when longer periods will be required to mark decidedly the progress which has been achieved. In due time also the Chemical Society will not fail to arrive at that stage; but to judge from the experience of the last year, we are still very far from having reached this stationary condition; on the contrary, although we may, with unmixed satisfaction, look back upon the achievements of the past—although we legitimately delight in the consciousness of our present strength—we derive from the very

rate of our growth, the right of considering ourselves in an early stage of development, permitting us still to indulge in the most youthful aspirations.

At no time during our past career, with the exception of our natal year, have we, between any two successive anniversary meetings, increased our body by a number of Fellows at all comparable with the increment on which I have to congratulate the Society this evening.

The present number of Fellows, as compared with the number at the last anniversary meeting, is as follows:—

Number of Fellows on March 30th, 1862		360
Fellows elected since that date	43	
„ deceased.....	2	
„ resigned.....	4	
Increase	—	37
Present number of Fellows		397
Number of Foreign Members on March 30th, 1862 ..		30
Members elected since that date	8	
„ deceased.....	1	
Increase.....	—	7
Present number of Foreign Members		37
Number of Associates on March 30th, 1862		14
Present number of Associates		10

On comparing the number of Fellows added to our list between the two last anniversaries (37), with the numbers who joined the Chemical Society between the two previous anniversaries (18), it is obvious that the rate of increment has more than doubled.

We have to deplore the loss, by death, of one of our distinguished foreign members, Dr. C. G. Lehmann, Professor of Chemistry in the University of Jena, and of two of our Fellows, Mr. F. E. Teschemacher, one of the founders of the Society, and Mr. M. Warton Johnson.

Carl Gotthelf Lehmann* was born at Leipzig, on March 7th, 1812. At the usual age he commenced the study of medicine

* This notice was kindly furnished by our Foreign Secretary.

in that city, and after taking an M.D. degree, became private tutor in the year 1837. In 1840 he published a small Manual of Theoretical Chemistry, which in 1856 had reached a sixth edition. In 1842 he was elected Extraordinary Professor of Medicine, and commenced in the same year his treatise on "Physiological Chemistry," which was completed within three years. This deservedly celebrated work, which reached a third edition in 1853, has been translated into English by the Cavendish Society, and exhibiting, as it does, extraordinary labour and research, is justly regarded as one of the most important contributions to this department of chemical literature.

In the year 1847, Dr. Lehmann became Professor of Physiological Chemistry in the Faculty of Medicine at Leipzig, and shortly afterwards published his "Elements of Physiological Chemistry," which was followed by several other works. After filling this chair for ten years, he was in 1857 induced to leave his native city, and to accept the Professorship of Chemistry in the University of Jena, a position which he held for the remainder of his life.

Although Professor Lehmann's literary labours undoubtedly represent his greatest achievements, and must have absorbed a considerable portion of that time which was not devoted to his duties as a teacher, yet, where problems requiring experimental investigation presented themselves, he was not deterred from undertaking their solution. His papers "On Human Urine in Health and Disease," "On Digestion," "On the amount of Carbonated Alkalis in Blood," "On the Organic Crystalline Constituents of Blood," "On the Presence of Sugar in Blood," "On the Formation of Sugar in the Liver," and on other subjects, sufficiently testify to his possession of the power to enlarge the boundaries of scientific knowledge by original investigation.

Frederick Edward Teschemacher* was the youngest surviving son of a Hanoverian gentleman, who settled in England about the middle of the last century. Educated with his brothers, by Dr. Lindsay, of Stoke Newington, the earlier portions of his active life were devoted to mercantile pursuits; but, in common with his elder brother, Mr. J. E. Teschemacher—who, afterwards, settling in the United States, was one of Dana's most zealous

* I am indebted to Mr. Denham Smith for the late Mr. Teschemacher's biography.

fellow-workers in discovering and describing the minerals of North America—his leisure time was given especially to mineralogy; this led him to the frequent use of the goniometer, with which he became a most expert and accurate observer. He was an early and assiduous student both of geology and botany, and frequent field-days gave him a knowledge of the *habitat* of most plants to be found within thirty miles of London. This early scientific training prepared him for the careful study of chemistry, to which, at the instance of many of his friends connected with the trade of the port of London, Mr. Teschemacher finally devoted himself. Maintaining his connexion with mercantile pursuits, he was constantly consulted respecting any new article of import, and the influence of this connexion may be clearly traced in his papers on Guano, Californian Gold-dust, and Gun-cotton, read before this Society, of which he was one of the founders, sharing first with its originator, Mr. Warington, the duties of secretary, and then taking the foreign secretaryship, until his gradually failing health compelled him to resign this office. Besides his contributions to this Society, a few papers, "On the Crystalline Form of some Salts," "On Chromate of Silver," &c., are to be found in the pages of the "Philosophical Magazine," to which he was an occasional contributor.

In 1836 Mr. Teschemacher married the eldest daughter of the late Richard Phillips, F.R.S. He passed a busy but not eventful life, honoured with the confidence of many who entrusted large pecuniary interests to his judgment, skill, and uprightness, whilst his calm, dispassionate temperament, conjoined with a clear judgment and much kindliness of heart, won the respect and esteem of all who were intimately acquainted with him. For many years a sufferer from asthma, he finally succumbed to its influence, quitting this life at Highbury, on the 10th of January last, in the 72nd year of his age.

Mr. Matthew Warton Johnson* commenced his education in the science of chemistry by private tuition under Mr. Joseph Nash. Having made himself familiar with the rudiments of the science, he entered as a pupil at University College, where he received the valuable instruction of the late Prof. Fownes, who held a high opinion of his ability. After studying at University

* The above obituary notice was supplied by Mr. Charles Tookey.

College, he went to the Royal College of Chemistry, where he carried out an examination of the sediment of the river Nile, and afterwards performed an elaborate investigation of xanthamylamide. Both papers are printed in the Journal of the Chemical Society. He also introduced to the notice of the Society a simple aspirator for laboratory use, an instrument which, more or less modified, has found considerable application. Its description is given in the Society's Journal of 1852. On leaving the Royal College of Chemistry, Mr. Johnson became lecture-assistant to Dr. Stenhouse at the laboratory of St. Bartholomew's Hospital. He eventually decided upon applying his knowledge to technical chemistry, and having become acquainted with a maker of printing-ink, Mr. Johnson was induced to devote his energies to the improvement of the substances used in its preparation. In this endeavour he so far succeeded, that a prize medal was awarded to the manufacturer, last year, by the Jurors of the International Exhibition, for the excellence of his printing-ink.

Mr. Johnson exercised a more than usual amount of order and neatness in all his experiments and investigations. "The labels of his bottles," to use the expression of one of his fellow-students, "invariably contained the full history of their contents, their birth, parentage, and education." He died on the 12th October, 1862, aged 35.

I have dwelt with some interest upon the rate of increment of our Society during the last year. Force in numbers, however, may be but a very fallacious criterion of the prosperity of a society, unless the work done be proportionate to the number. The task of the Chemical Society is the promotion by earnest research of the science of chemistry. To form an adequate estimate of our vitality, we have, therefore, not only to consider the expansion of our list of members, but also, and indeed chiefly, the influence which our united efforts have exercised upon the advancement of experimental science, *i.e.*, the number and value of the papers which we have been able to collect. In this respect, also, the Proceedings of the Society evince decided progress, and we cannot but congratulate ourselves on the unintermittent flow of interesting contributions which have continued to form the attraction of our meetings. Subjoined is a list of the papers read before the Society.

List of Papers read at the Meetings of the Chemical Society from March 31, 1862, to March 30, 1863 :—

1. "On the Production of a Blue Substance by the Electrolysis of Sulphate of Aniline :" by H. Letheby, M.B., M.A., Ph. D.
2. "On the Action of Carbonate of Ammonium on Magnesia-salts :" by Dr. Edward Divers.
3. "On the Action of Mordants upon Cotton-fibre :" by Walter Crum, F.R.S.
4. "On the Capacity of Arsenious Acid for Bases, and on certain Arsenites :" by Charles L. Bloxam.
5. "On Reciprocal Decomposition among Salts in Solution :" by Dr. Gladstone, F.R.S.
6. "On the General Occurrence of Titanic Acid in Clays :" by M. E. Riley.
7. "On the Composition of the Amorphous Deposit of Urates in Healthy Urine :" by H. Bence Jones, M.D., F.R.S.
8. "Note on Perchloric Ether :" by H. E. Roscoe.
9. "On the Composition of the Aqueous Acids of Constant Boiling Point :" (second communication) by H. E. Roscoe.
10. "On Sombrerite :" by Dr. T. L. Phipson, F.C.S.
11. "Note on the Sulphur-compound formed by the Action of Sulphuretted Hydrogen on Formate of Lead at a High Temperature :" by W. J. Hurst.
12. "Description of a Combined Maximum and Minimum Mercurial Thermometer :" by W. Symons.
13. "On Berberine : Contributions to its History, and Revision of its Formula :" by W. D. Perrins.
14. "On a Complex Cyanide of Iron, Copper, and Potassium :" by William T. Wonfor.
15. "On the Formation of the Iodides of the Alcohol-radicles from Boghead Naphtha :" by Greville Williams.
16. "On the Separation of Tin from Antimony, and on the Analysis of Alloys containing Lead, Tin, Antimony, and Copper :" by Charles Tookey.
17. "On a Method for the Determination of Nitric and Nitrous Acids :" by A. Vernon Harcourt, M.A.
18. "On the Hydrides of the Alcohol-radicles existing in the Products of the Destructive Distillation of Cannel Coal :" by C. Schlorlemmer.
19. "On the Constitution of Melampyrin :" by Dr. Erlenmeyer and J. A. Wanklyn.

20. "On a Volumetric Process for the Analysis of Water:" by E. Nicholson, F.C.S.
21. "On the Composition of the Amorphous Deposit in Healthy Urine:" Note by Professor Heintz to Dr. H. Bence Jones.
22. "On Hypobromous Acid:" by William Dancer.
23. "On the Formation of Organo-metallic Radicles by Substitution:" by G. B. Buckton.
24. "On the Specific Gravity of Urine as a measure of its Solid Constituents:" by E. Nicholson.
25. "Note on Certain Processes of Rock-formation:" by Arthur H. Church.
26. "On the Determination of the amount of Organic Matter in Drinking Water by means of a Standard Solution of Permanganate of Potash:" by Dr. Woods.
27. "On the Effect of Heating Sulphate and Sulphide of Lead in Hydrogen and Carbonic Oxide:" by G. F. Rodwell.
28. "On the Composition of Gall-stones;" Dy Dr. Thudichum.
29. "On the Solvent Power exercised by a solution of Hyposulphite of Soda upon many Salts insoluble in Water:" by F. Field.
30. "On the Atomic Weight of Cobalt:" by W. J. Russell.
31. "On the Action of Sulphuric Acid upon Lead:" by F. Crace Calvert and R. Johnson.
32. "On the Formation of Phenic and Benzoic Acids from Benzol:" by A. H. Church, B.A.
33. "Analysis of Red Chalk:" by A. H. Church, B.A.
34. "On the Atomic Weight of Nickel:" by Dr. W. J. Russell.
35. "On the Bicarbonate of Ammonia of the Chinca Isles:" by Dr. T. L. Phipson.
36. "Remarks on the Proposed Application of the Soap-test to the Quantitative Analysis of Water:" by Dr. B. H. Paul.
37. "On Formamide:" by Dr. Hofmann.
38. "On the Chinoline and Leucoline Series:" by C. Greville Williams.
39. "On the Spontaneous Conversion of Gun-cotton into Pectic and Parapectic Acids:" by Dr. Edward Divers.
40. "Note on Oxamide:" by Dr. Attfield.

From the preceding list, it appears that the Chemical Society has received, during the last twelve months, a greater number of contributions than in any previous year of its existence.

The discourses delivered at the meetings of the Society have also been more numerous during the last session than formerly. The interest and variety of the subjects treated of may be estimated by a glance at the subjoined enumeration.

List of discourses delivered at the meetings of the Chemical Society between March 31st, 1862, and March 30th, 1863 :—

1. "On the Influence of the Quantitative Method on the Development of Scientific Chemistry :" by Dr. Debus.
2. "On the Chemistry of Opium :" by Dr. Thomas Anderson.
3. "On Vapour-densities :" by M. H. Sainte-Claire Deville.
4. "On Oxide of Ethylene, considered as a link between Organic and Mineral Chemistry :" by M. A. Wurtz.
5. "On the Chemistry of Digestion :" by Dr. Marcet.
6. "On the Assimilation of Nitrogen by Plants :" by Dr. Gilbert.

In the delivery of these evening discourses, which have never failed to attract crowded audiences to the rooms of the Society, an innovation has taken place, on which I cannot refrain from congratulating the members, as peculiarly befitting the celebration of the Grand International Congress of Industry, which has marked the year 1862. I allude to the delivery of lectures by foreigners in their respective tongues. The field was brilliantly opened by two of our most distinguished foreign members, M. H. Sainte-Claire Deville and M. A. Wurtz, whose eloquent addresses in French will not easily be forgotten by those who had the good fortune of hearing them. The importance of this innovation will not be underrated. I welcome it as an early fruit of the beneficial influence which the great institution of international exhibitions has already exercised upon the mutual relations of different countries. This innovation involves the admission of a great principle. In establishing, once for ever, these international chemical discourses at its meetings, the Chemical Society has loudly proclaimed the cosmopolitan character of science, and that henceforth it will look upon the several nations engaged in scientific pursuits, as upon so many federal members of a great republic, united by the love of science, and pledged, by contributions to a common treasury, as it were, to uphold its cause and raise its dignity.

The establishment of international lectures is not the sole benefit which the Chemical Society has derived from the Industrial Congress of all Nations during last year. The Exhibition had brought us an assemblage of illustrious chemists such as the metropolis had never witnessed before; indeed, we have had an opportunity of receiving, in rapid succession, the majority of our distinguished foreign members, many of whom appeared for the first time at the meetings of the Chemical Society.

On the same evening, the registers of the Society were signed by such men as Professor H. Sainte-Claire Deville, of Paris; Professor Fritzsche, of St. Petersburg; Professor Schrötter, of Vienna; and Professor A. Wurtz, of Paris. The usual presence of so many distinguished visitors, not unfrequently of the very captains of our science—of men, whose names have become household words in the mouths of chemists—conferred upon our meetings during last summer a charm and interest which was felt by all who attended them. It was, no doubt, under feelings of international good fellowship thus created, that the Society, at their last meeting before the autumnal vacation, made so large an addition to the list of our foreign members, when the labours of this extraordinary session were fitly brought to a conclusion by inscribing upon our rolls the names of the following distinguished chemists: Messrs. Canizzaro, University of Palermo; Kekulé, University of Ghent; Loewig, University of Breslau; Malaguti, Faculty of Rheims; Marignac, Geneva; Pasteur, Ecole Normale, Paris; Stas, Military School, Brussels; and Zinin, University of St. Petersburg.

The unprecedented activity in the several departments of chemistry and the collateral sciences, to which I had an opportunity of alluding when addressing you at our last anniversary, has by no means abated during the twelve months just elapsed; but among the numerous chemical results which have rewarded the exertions both of physicists and chemists, there are but very few which, in importance, could be compared with the achievements of 1861. The scientific movement of 1862, consists, in a measure, in secondary waves, following the powerful agitation which the grand discoveries of 1861 and 1860 had imparted to the steady stream of chemical research. A vast number of, partly at all events, most valuable inquiries, both physical and chemical, have followed the brilliant conquests for which we are indebted to the

labours of Plücker, and the grand researches of Kirchhoff and Bunsen. The method of analysis by spectrum observation, which has opened an entirely new field of investigation, has been further elaborated during the last year. Considerable progress has been made in the study of the principles involved in this form of inquiry, in determining the simplest mode of experimenting; and, lastly, in the development of the important results already obtained by this new method, viz., the further investigation of the newly-discovered elements—cæsium, rubidium, and thallium. The intense interest awakened by the achievements of spectral analysis, has opened the archives of science, and brought to light the earlier researches carried out in this direction; and, with the documents thus rescued, I might almost say from oblivion, the history of this new branch of chemical physics may now be traced to its very origin.

The dialytic methods of analysis introduced by one of our Fellows have been not less actively improved and expanded; the usefulness of dialysis for the purpose of separating mixtures, and preparing substances in a state of absolute purity, is conspicuously illustrated by the daily growing number of its applications.

The narrow outlines which limit this report, preclude the possibility of more than an attempt at singling out from the tide of purely chemical researches, a few inquiries which appear to rise above the general level. In the department of inorganic chemistry, our attention is fixed by the researches which the indefatigable Schönbein prosecutes with so much vigour, and more especially by an observation of his, according to which, nitrogen and water, under certain conditions, appear capable of joining into nitrite of ammonium. In endeavouring to trace some of the more important steps in the field of organic chemistry, I may be allowed briefly to allude to the beautiful results which Kolbe continues to obtain by the consistent prosecution of views by no means shared by the majority of chemists; to Kekulé's further expansion of his inquiry into the nature of organic acids, a subject which of late has also been cultivated by Cahours; to the researches of Wurtz and Berthelot on hydrocarbons and alcohol-like bodies, which promise to throw light upon many cases of isomerism hitherto obscure; to the further examination, by one of our colleagues, of the derivatives of zinc-ethyl; to the elucidation which the group of sugars and sugar-like bodies has received by the investigations of Linnemann, Erlenmeyer, Luynes, and several

Fellows of our Society; and, lastly, to the remarkable experiments of Mendius on the transformation of the nitriles into alcohol-bases, under the influence of nascent hydrogen. In physiological chemistry, Pettenkofer's experiments on respiration, carried out upon an hitherto unprecedented scale, have attracted general attention.

Such are some of the more prominent scientific subjects which the last year has brought into notice; but it would not be right to bring this slight and fragmentary sketch to a conclusion, without pointing to the progress, rapid and important, of all the arts and manufactures based upon chemical discovery. This progress was conspicuously illustrated by the International Exhibition of 1862, in the survey of which the observer cannot have failed to be struck by the rapidity with which industry at the present day, and in this country more particularly, assimilates the discoveries of science, gathering, to express it in words I made use of on another occasion,* the ripe fruit of practical result from the seedling of theory only just sprung into existence, seizing upon new laws ere yet fairly ripe for enunciation, and boldly founding great manufactures upon laboratory researches, themselves still incomplete. So closely, indeed, does practice now tread upon the heels of theory, and so eager is the competition of manufacturers to turn the conquests of science to immediate technical account, that the philosophical chemist is often quite outrun, and wonders to find, as the unexpected result of his purely scientific researches, industrial improvements which he did not himself foresee, and often cannot fully explain.

In speaking of the progress of chemistry, scientific and industrial, I should, indeed, ill perform my duty were I to omit dwelling for a moment upon a subject in which the members of the Chemical Society, as a body, must feel the liveliest interest. I allude to the ample share of public recognition conferred upon many of our colleagues during the past year. Quite a shower of medals has fallen upon members of the Society who had contributed to the International Exhibition. Several members, among them the discoverer of thallium, have been encouraged in the prosecution of their labours by liberal grants from the Royal Society. One of the Royal medals has rewarded the brilliant researches of the

* Report on the Chemical Products contributed to the International Exhibition of 1862.

distinguished chemist into whose hands I am going to resign my office this evening. Lastly, one of the former occupants of this chair, the celebrated philosopher whom unanimous consent has long placed at the head of the chemists of this country, has earned, within the short space of a single month, the highest scientific distinctions which England and France are able to bestow.

When addressing you last year, I gave a full account of the changes which your Council, after mature consideration, deemed advisable to introduce into the publications of our Journal. I have explained the reasons which led them to substitute a Monthly for the Quarterly Journal previously published. The Journal in its new form, I am happy to say, has given general satisfaction, all the anticipated advantages having been fully realized. The frequency and regularity of its appearance has secured to our contributors a rapidity of publication hitherto unknown in the history of the Chemical Society, while the increased number of sheets has enabled us to publish abstracts of all the important chemical papers scattered throughout the Proceedings and Transactions of the several learned societies in Great Britain. A combination of so many improvements could not remain without beneficial results; and the Fellows will hear, with unmixed satisfaction, that the new arrangement has not only brought us an increased number of contributors, but also considerably augmented the sale of the Journal. I shall not touch upon the financial condition of the Society, leaving to our excellent Treasurer the undivided pleasure of submitting to you the balance-sheet of the financial year that has just ended. But I may be permitted to mention some facts connected with the Journal which speak for themselves. Early in December last, the Council decided to print henceforth 750 copies of the Journal instead of 600, which was the number formerly printed. Again, in the beginning of the year, it was agreed that the time had arrived for starting a new series, the publication of which, under the auspices of our indefatigable Editor, has actually commenced.

In the preceding remarks, Gentlemen, I have alluded to the several topics which, as President of the Chemical Society, I had to bring under your notice. To complete the proceedings of the evening, our Treasurer will give you a financial statement of the

affairs of the Society, and you will then be called upon to ballot for the officers of the ensuing year.

And now, Gentlemen, on relinquishing this chair, nothing more remains except the pleasant duty of expressing to the Council, the officers, and to you all, my cordial thanks for the uniform courtesy and kind indulgence I have ever experienced at your hands, since you have done me the honour of electing me President of the Chemical Society.

The following gentlemen were elected as Council and Officers for the ensuing year:—

President.—Alexander W. Williamson, Ph.D., F.R.S.

Vice-Presidents who have filled the Office of President.—W. T. Brand, F.R.S., Sir B. C. Brodie, F.R.S., C. G. B. Daubeny, M.D., F.R.S., Thomas Graham, F.R.S., A. W. Hofmann, LL.D., F.R.S., W. A. Miller, M.D., F.R.S., Lyon Playfair, Ph.D., C.B., F.R.S., Colonel Philip Yorke, F.R.S.

Vice-Presidents.—Walter Crum, F.R.S., H. Bence Jones, M.D., F.R.S., Alfred Smee, F.R.S., Robert Warington, Esq.

Secretaries.—Theophilus Redwood, Ph.D., William Odling, M.B., F.R.S.

Foreign Secretary.—E. Frankland, Ph.D., F.R.S.

Treasurer.—Warren De la Rue, Ph.D., F.R.S.

Other Members of the Council.—F. A. Abel, F.R.S., Thomas Andrews, M.D., F.R.S., H. Debus, Ph.D., F.R.S., J. B. Lawes, F.R.S., George H. Makins, Esq, A. Matthiessen, Ph.D., F.R.S., Hugo Müller, Ph.D., A. R. Normandy, Esq., David S. Price, Ph.D., H. E. Roscoe, Ph.D., F.R.S., W. J. Russell, Ph.D., John Stenhouse, LL.D., F.R.S.

Librarian.—Henry Watts, B.A., F.R.S.

Collector.—Mr. Thomas West, Burlington House.

The thanks of the meeting were voted to the President, Officers, and Council for their services to the Society during the past year.

THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON.

Dr. **Cr.**

1862-3.		£	s.	d.	1862-3.		£	s.	d.	£	s.	d.
March 25.	To Cash on hand		597	17	8	Journal.	By Editor's Salary to 25th March, 1863		95	0	0	
Sept. 4.	„ Half-yearly Dividend on £600 Consols, less Income-tax		8	13	3		„ Printing Journal		221	16	8	
1863.							„ Distributing ditto		32	17	0	
March.	„ Half-yearly Dividend on £800 Consols, less Income-tax		11	11	0		„ Advertising ditto		6	1	0	
	„ Sale of Journals		33	2	8		„ Translating (Mr. Watts)		9	5	0	
	„ Sundry Receipts from March 25th, 1862, to March 25th, 1863, as below:—						„ Wilson & Bristow's Draft of Agreement		3	3	0	
										368	2	8
	Life Compositions	130	0	0	Library.		„ Librarian's Salary to 25th March, 1863		25	0	0	
	Admission Fees	72	0	0			„ Proceedings of Royal Society		50	0	0	
	Resident Members' Subscriptions previous to 1862	10	0	0			„ Books and Magazines		22	4	8	
	Non-resident Members' Subscriptions previous to 1862	12	0	0			„ Subscription to Cavendish Society		1	1	0	
	Resident Members' Subscriptions for 1862	62	0	0	Collector and Clerk.		„ Collector's Commission		34	14	0	
	Non-resident Members' Subscriptions for 1862	24	0	0			„ Clerk		3	0	0	
	Resident Members' Subscriptions for 1863	298	0	0	General Printing.		„ Harrison & Son's account		71	15	7	
	Non-resident Members' Subscriptions for 1863	85	0	0	Receipt Books, Stationery, &c		„ Receipt Books, Circulars, &c.		5	13	5	
	Non-resident Members' Subscriptions for 1864	1	0	0			„ Postage Envelopes		4	2	10	
							„ Receipt Stamps, per W. West		0	16	6	
							„ Stamps		0	3	5	
					House Expenses.		„ Royal Society, Share of Tea Expenses		12	16	2	
							„ Thos Hux, 1 Year's Salary to 25th March, 1863		20	0	0	
							„ „ Gas, Petty Cash, &c.		4	4	9	
							„ Wm. Page, Cleaning		1	1	0	
							„ Gate Porter		2	2	0	
					Furniture.		„ T. Fox, Blinds for Diagrams		14	12	0	
					1862. June 25.		„ Purchase of £200 3 per cent. Consols		184	0	0	
							„ Balance at Coutts'					
			694	0	0					519	14	7
		£	1345	4	7		£			1345	4	7

Assets	£	s.	d.
Balance at Messrs. Coutts	519	14	7
Invested in 3 per cent. Consols	800	0	0
	£1319	14	7

Examined and found correct, GEO. D LONGSTAFF, THOS. TAYLOR, JOHN J. GRIFFIN

London, March 26th, 1862.

April 2nd, 1863.

Dr. Hofmann, Vice President, in the chair.

James Mungo Brown, Esq., was elected a Fellow of the Society.

A paper was read entitled—

"Contributions to the History of the Tolyl Series:" by M. Eugene Sell, of Bonn.

April 16th, 1863.

Dr. Williamson, President, in the chair.

The following were elected Fellows of the Society:—
L. F. Vernon Harcourt, B.A., 47, Cadogan Place.
H. Salt, Esq., 29, Gordon Square.

The following papers were read:—

"On some Derivatives of Naphthylamine:" by Messrs. Perkin and Church.

"On Vanadium Ochre:" by Dr. Phipson.

"On the Chloromaleic Acid obtained from Tartaric Acid:" by Mr. W. H. Perkin.

Dr. Hofmann gave an account of the Decomposition of Benzidine by Distillation.

May 7th, 1863.

Dr. Williamson, President, in the chair.

Dr. Thomas Wood was elected a Fellow of the Society.

A paper was read,—

"On Pickeringite:" by Dr. How.

Dr. Hofmann gave a further explanation of the Decomposition of Benzidine by Distillation, to which he had referred at the previous meeting.

Dr. Lyon Playfair delivered a lecture "On the Constitution of Salts."

May 21st, 1863.

Dr. Williamson, President, in the chair.

Samuel Parr, Esq., Nottingham, and John Ewen Davidson, B.A., 16, Mansfield Street, Portland Place, were elected Fellows of the Society.

A paper was read,—

"On the Derivatives of Hydride of Heptyl:" by Mr. C. Schorlemmer.

Dr. Hofmann announced that Aniline-blue is a derivative of Rosaniline, in which three atoms of hydrogen are replaced by three atoms of phenyl.

Mr. Grove, Q.C., delivered a lecture on the "Effects of Intense Heat on Fluids."

June 4th, 1863.

Dr. Williamson, President in the chair.

Mr. Wanklyn gave an account of a research by himself and Dr. Erlenmeyer, "On the Hexyl-group."

Professor Berthelot, of Paris, delivered a lecture "On Synthetic Methods in Organic Chemistry."

June 18th, 1863.

Dr. Williamson, President, in the chair.

The following were elected Fellows of the Society:—

Rev. Thomas Neville Hutchinson, M.A., King Edward's School, Birmingham; C. Poole, Esq., Scholar of Exeter College, Oxford; Dr. Alexander Martius, Royal College of Chemistry; James Scorgie, Esq., General Assembly's Institution, Bombay.

Dr. Frankland made a verbal communication "On the Atomic Weight of Cæsium."

The following papers were read:—

"On a curious instance of Electrolytic Action:" by Professor Abel.

"Note on some Metamorphoses of Oxalic Acid:" by A. H. Church, B.A.

"Note on the Quantitative Determination of Phosphoric Acid by Salts of Magnesia:" by Mr. Robert Warington, Jun.

"On the Synthesis of Certain Series of Organic Compounds:" by Mr. Calton, B.A.

"On the Iodide of Iodammonium:" by Professor F. Guthrie.

November 5th, 1863.

Dr. Hofmann, Vice-President, in the chair.

Mr. J. Whitfield, of Scarborough was elected a Fellow of the Society.

The following papers were read:—

"On the Detection of Nitric Acid:" by Dr. Sprengel.

"On the Variations of Hippuric Acid in Human Urine:" by Dr. Thudichum.

"On Azuline:" by Mr. S. Piesse.

November 19th, 1863.

Dr. Williamson, President, in the chair.

The following papers were read:—

"On the Occurrence of Vanadium in English Pig-iron:" by Mr. E. Riley.

"On a New Method of Producing the Mercury-compounds of the Alcohol-radicles:" by Dr. Frankland and B. F. Duppa, Esq.

"On an Apparatus for evolving Sulphuretted Hydrogen:" by Dr. Phipson.

"On the Constitution of the so-called Alcohol-radicles:" by Mr. Schorlemmer.

December 3rd, 1863.

Dr. Williamson, President, in the chair.

The following were elected Fellows of the Society:—

J. L. Bell, Esq., Newcastle on Tyne; Richard Crossly, Esq.,

Alexandria by Dumbarton; Rev. T. T. Jones, St. Dogmael's, Cardigan; Nathaniel Levett, Esq., St. George's Hospital; John Pattinson, Esq., Newcastle-on-Tyne; Andrew Neill Rae, Esq., Bonhill by Dumbarton; William Vaughan Russell, Esq., Portland Place, Leamington.

The following papers were read:—

"Note on the Quantitative Determination of Sulphur:" by Dr. David S. Price.

"On Essential Oils:" by Dr. Gladstone.

"On a New Reaction for the Production of the Zinc-compounds of the Alcohol-radicles:" by Dr. Frankland and B. F. Duppa, Esq.

December 17th, 1863.

Dr. Williamson, President, in the chair.

The following were elected Fellows of the Society:—

T. J. Glass, Esq., Cheltenham; James Duncan, Esq., 5, Highbury Hill, Highbury; Rev. Burford Waring Gibsone, M.A., Mercers' School, College Hill; James Scotson, Esq., College, Chester; B. F. Duppa, Esq., Hollingbourne House, near Maidstone.

A paper was read "On a new form of Gas Combustion Furnace:" by Mr. Wm. Herapath.

Dr. Frankland described a case of Spontaneous Ignition which occurred in Condensing Oxygen-gas in an iron receiver.

Donations to the Library in the year 1863:—

"On the Manufacture of Caustic Soda:" by A. Norman Tate: from the Author.

"Remarks on the recent Eruption of Vesuvius, in December, 1862:" by Dr. Daubeny: from the Author.

"Contributions to the American Journal of Science and Art, for the year 1862:" by M. Carey Lea: from the Author.

"The Art of Perfumery:" by G. W. S. Piesse.

"The Laboratory of Chemical Wonders:" by the same: from the Author.

"On the Carbonates of Alumina, Glucina, and the Sesquioxides

of Chromium and Iron:" by Theodore Parkman, Ph. D.: from the Author.

"A Dictionary of Chemistry and the Allied Branches of other Sciences:" by Henry Watts. Parts I.—X. from Messrs. Longman and Co.

"Lectures on the Coal-tar Colours, and on Recent Improvements in Dyeing and Calico-printing:" by F. Crace Calvert: from the Author.

"On the Impurities of Commercial Zinc, with Special Reference to the Residue insoluble in Dilute Acids, to Sulphur and to Arsenic:" by C. W. Elliot and F. H. Storer: from the Authors.

"On Phosphorescence:" by T. L. Phipson, Ph.D.: from the Author.

"A Tract on Crystallography, designed for the Use of Students in the University:" by W. H. Miller, M.A., Cambridge, 1863: from the Author.

"Climate: an Inquiry into the Causes of its Differences, and into its Influence on Vegetable Life:" by Dr. Daubeny: from the Author.

"Rothamsted Memoirs:" 2 vols. 8vo.: by J. B. Lawes and J. H. Gilbert: from the Authors.

"Memoirs on the Chemistry of Animal and Vegetable Growth:" by J. B. Lawes, J. H. Gilbert, and E. Pugh: from the Authors.

"Drawing and Plans of the Lawes' Testimonial Laboratory, Rothamsted:" from J. B. Lawes, Esq.

"Catalogue of the Army Medical Museum at Washington:" from the Surgeon-General of the United States Army.

"Report of Lieut.-Colonel J. D. Graham, Topographical Engineer, (U.S.) on Mason and Dixon's Line:" from the Author.

"The Use of Salt in Agriculture:" Prize Essays: published by the Salt Chamber of Commerce of Northwich: by Robert Falk and T. L. Phipson: from Dr. Phipson.

"Reports by the Juries of the International Exhibition of 1862, Class II., Section A., Chemical Products and Processes:" A. W. Hofmann, Reporter: from Dr. Hofmann.

"Johannis Mayow Opera omnia medico-physica:" Hagæ-Comitium, 1681: from G. F. Rodwell, Esq.

"Recherches sur les Tungstates, les Fluotungstates et les Silicotungstates:" par C. Marignac: from the Author.

"Recherches sur les composés polyatomiques;" par A. V. Lourenço: from the Author.

"Dell' Azione chimica dell Acqua sopra i Sali e sopra gli Acidi:" di Paolo Peretti: from the Author.

"Memoria di Paola Peretti, Sopra un lavoro chemico, &c. da C. F. Schönbein, con il titole: Rapporti dell' Ossigeno ozonnizato con la Chimica practica:" from the Author.

"Ausführliches Lehrbuch der Organischen Chemie, von Dr. Hermann Kolbe, Band I. and Band II., Lieferung I.—IV.:" from the Author.

Denkrede auf Joh. Andreas von Wagner, gehalten in der äffentlichen Sitzung der königl.-baeyerischen Akademie der Wissenschaften, am 28 Nov., 1862:" von Dr. C. F. Ph. von Martius: from the Academy.

"Rede in der öffentlichen Sitzung der konigl.-baeyerischen Akademie der Wissenchaften, am März, 1862, zur Feier ihres 104ten Sitzungstages: gehalten von Justus Freiherrn von Liebig:" from the Academy.

"Somatologie, oder Lehre von der inneren Beschaffenheit der Körper:" von Dr. J. V. Hofmann: from the Author.

"Das Chemische Laboratorium der Universität Christiania:" herausgegeben von A. Strecker: from the Royal University of Norway.

"Geologiske Undersögelser i Bergens Omegn:" af. Th. Hiortduhl og M. Irgens.

"Om Kometbanernes indbyrdes Beliggenhed;" af H. Mohn.

"Om Cirklers Berφring:" af C. M. Guldberg.

"Beskrivelse over *Lophogaster typicus*: af Dr. Michael Sars."

"Om *Siphodentalium vitreum*, en ny slegt og Art af Dentalidernes Familie:" af Dr. Michael Sars:
from the Royal University of Norway.

Periodicals:—

"Memoirs of the Royal Astronomical Society," 1861–2.

"Monthly Notices of the same," Nov., 1862, Dec., 1863:
from the Society.

"Quarterly Journal of the Geological Society for 1863:"
from the Society.

"Proceedings of the Royal Institution of Great Britain" (1861–2); also vol. IV., Pt. 2.

"Lists of the Members, Officers, &c., of the Royal Institution for the years 1861, 1862, and 1863:" from the Royal Institution.

"Pharmaceutical Journal" for 1863: from the Editor.

"Chemical News," Nos. 168–208: from the Editor.

"Journal of the Society of Arts," Nos. 525—576: from the Society.

"The Mining and Smelting Magazine," Jan.—Dec., 1863: from the Editor.

"Journal of the Photographic Society," Jan.—Dec., 1863: from the Society.

"Annual Report of the Yorkshire Philosophical Society," for 1862: from the Society.

"Calendar for the year 1863 of the Science and Art Department of the Committee of Council on Education:" from the Department.

"The Reader; a Review of Current Literature;" Nos. 1—49: from the Editor.

"London Review," Nos. 129—139: from the Editor.

"The Parthenon," Nos. 39—49: from the Editor.

"The Sculptors' Journal," Nos. 1, 2, 3: from the Editor.

"Transactions of the Royal Society of Edinburgh," Vol. XXIII, Part 2.

"Proceedings of the same" (sessions 1862–3): from the Royal Society of Edinburgh.

"The Atlantis," Nos. 7 and 8: from the Catholic University of Ireland.

"The Canadian Naturalist and Geologist" (1862): from the Natural History Society of Montreal.

"Smithsonian Reports for the year 1861:" from the Smithsonian Institution at Washington.

"American Journal of Science and Arts," Nov., 1862—Sept., 1863: from the Editors.

"Transactions of the American Philosophical Society" (new series), vol. xii., parts 2—3.

"Proceedings of the same," Jan.—Dec., 1862: from the Society.

"Journal of the Franklin Institute," Jan.—Sept., 1863: from the Institute.

"Proceedings of the Academy of Natural Sciences at Philadelphia," 1862, Nos. 7—12; 1863, Nos. 1, 2, 3: from the Academy.

"Proceedings of the American Pharmaceutical Association" (1862): from the Association.

"Les Mondes; Revue hebdomadaire des Sciences; par l'Abbé

Moigno," Tome i., et Tome ii., Livraison 1—15: from the Editor.

"Bulletin de la Classe des Sciences de l'Academié Royale de Belgique," 1863: from the Academy.

"Annuaire de l'Academie Royale de Belgique" (1861): from the Academy.

"Denkschriften der kaiserlichen Akademie der Wissenschaften in Wien (math.-naturw. Classe), Band XXI.

Sitzungsberichte derselben:

"Erste Abtheilung." Bände xlv., xlvi., and xlvii., Hefte 1, 2, 3.

"Zweite Abtheilung," Bände xlv., Heft 5; Bd. xlvi, xlvii.

from the Imperial Academy of Sciences at Vienna.

"Abhandlungen der königlich.-baeyerischen Akademie der Wissenschaften in München (math.-phys. Classe), Band ix., Abtheilung 3:" from the Royal Bavarian Academy of Sciences.

"Sitzungsberichte derselben," 1861, Bande 2, Heft. 3; 1863, Bd. 1. Heft. 3: from the Royal Bavarian Academy of Sciences.

"Verhandlungen der naturforschenden Gesellschaft in Basel. Dritter Theil, 4tes. oder Schluss-Heft." (1863): from the Society.

"Jahrbuch der königl.-kaiserlichen geologischen Reichsanstalt zu Wien," Band. 2, Nro. 1: from the Geological Institute of Vienna.

"General Register derselben," Bünde 1—10: from the Geological Institute of Vienna.

"Zeitschrift fur Chemie und Pharmacie:" herausgegeben von Dr. E. Erlenmeyer, Sechster Jahrgang, Heft. 1—8: from the Editor.

"Öfversigt af Kongl, Vetenskaps Akademiens Forhandlingar Nittonde Årgången," 1862:

from the Royal Academy of Sciences at Stockholm.

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ERRATA.

P. 80, line 7 from bottom, *for* 2· *read* 0·2.
P. 81, line 22, from bottom, *dele* "9·74 grains carbonate of magnesia."
P. 102, line 3, *for* Bouissingault, *read* Boussingault.
P. 107, line 4 from the bottom, *for* assimilation of nitrogen, *read* assimilation of free nitrogen.
P. 108, line 2 after Table V, *for* computed, *read* competent.
P. 120, line 4 from the bottom of the Table, *for* 0·0880, *read* 0·0490; line 2 from the bottom of the Table, *for* − 0·0040, *read* − 0·0480; last line of Table, *for* + 0·1320, *read* 0·0850; and *for* 1·5, *read* 1·3; last line of page, *for* 0·285, *read* 0·258.
P. 121, line 8, *for* 40–50 fold, *read* nearly 90 fold.
P. 126, line 5 of fourth paragraph, *for* free or uncombined nitrogen, *read* free or combined nitrogen.
P. 136, line 9, *for* (fig. ii, plate), *read* (fig. i, plate ii).
P. 158, line 1 of last paragraph, *for* The mixtures: with, *read* The mixtures with.
P. 168, line 2 from bottom, *for* had had been, *read* had been.

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